SUPPLEMENTARY INFORMATION

Bespoke Photoreductants: Tungsten Arylisocyanides

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EXPERIMENTAL SECTION

Synthesis of N-formyl-4-bromo-2,6-diisopropylaniline. Acetic anhydride (40 mL, 422.7 mmol) was cooled to 0 °C and formic acid (20 mL, 530.1 mmol) was added *via* syringe over 10 minutes. The colorless solution was allowed to warm to room temperature, then heated at 50 °C for 2 hours. The solution was then allowed to cool to room temperature and then cooled to 0 °C. 4-bromo-2,6-diisopropylaniline was added *via* syringe, and the mixture was then allowed to warm to room temperature. The mixture was allowed to stir for 30 minutes, then cooled to 0 °C, followed by the addition of 0 °C H_2O (*ca.* 300 mL), resulting in the formation of a light pink suspension. The mixture was filtered, and the precipitate was washed with H_2O (*ca.* 1 L). The white precipitate was dried *in vacuo* overnight to give N-formyl-4-bromo-2,6-diisopropylaniline (5.05 g, 76%) as a white solid. Mixture of isomers ^{1}H NMR ($CDCl_3$): 1.16 [d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, ($\underline{Me}_2CH)_2C_6H_2Br(NHCHO)$], 1.18 [d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, ($\underline{Me}_2CH)_2C_6H_2Br(NHCHO)$], 3.04 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H, ($Me_2C\underline{H})_2C_6H_2Br(NHCHO)$], 3.16 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H, ($Me_2C\underline{H})_2C_6H_2Br(NHCHO)$], 7.21 [b, 1H, $(Me_2CH)_2C_6H_2Br(N\underline{H}CHO)$], 7.28 [s, 2H, $(Me_2CH)_2C_6\underline{H}_2Br(NHCHO)$], 7.30 [s, 2H, $(Me_2CH)_2C_6\underline{H}_2Br(NHCHO)$], 7.91 [d, $^3J_{H\text{-}H}$ = 12 Hz, 1H, $(Me_2CH)_2C_6H_2Br(N\underline{H}CHO)$], 7.97 [d, $^3J_{H\text{-}H}$ = 12 Hz, 1H, $(Me_2CH)_2C_6H_2Br(NHC\underline{H}O)$], 8.38 [d, $^3J_{H\text{-}H}$ = 1 Hz, 1H, $(Me_2CH)_2C_6H_2Br(NHC\underline{H}O)$]. Mixture of isomers $^{13}C\{^1H\}$ NMR ($CDCl_3$): 23.5 [s, 4C, ($\underline{Me}_2CH)_2C_6H_2Br(NHCHO)$], 23.5 [s, 4C, ($\underline{Me}_2CH)_2C_6H_2Br(NHCHO)$], 28.7 [s, 2C, ($Me_2\underline{C}H)_2C_6H_2Br(NHCHO)$], 29.0 [s, 2C, ($Me_2\underline{C}H)_2C_6H_2Br(NHCHO)$], 123.1 [s, 1C, $(Me_2CH)_2\underline{C}_6H_2Br(NHCHO)$], 123.2 [s, 1C, $(Me_2CH)_2\underline{C}_6H_2Br(NHCHO)$], 127.1 [s, 2C, $(Me_2CH)_2\underline{C}_6H_2Br(NHCHO)$], 127.3 [s, 2C, $(Me_2CH)_2\underline{C}_6H_2Br(NHCHO)$], 128.9 [s, 1C, $(Me_2CH)_2\underline{C}_6H_2Br(NHCHO)$], 129.4 [s, 1C, $(Me_2CH)_2\underline{C}_6H_2Br(NHCHO)$], 148.6 [s, 2C, $(Me_2CH)_2\underline{C}_6H_2Br(NHCHO)$], 149.2 [s, 2C, $(Me_2CH)_2\underline{C}_6H_2Br(NHCHO)$], 160.8 [s, 1C, $(Me_2CH)_2C_6H_2Br(NH\underline{C}HO)$], 165.5 [s, 1C, $(Me_2CH)_2C_6H_2Br(NH\underline{C}HO)$].

Spectroscopic data for 2,6-diisopropylphenylisocyanide. ^{1}H NMR (C_6D_6): 1.06 [d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, ($\underline{Me}_2CH)_2C_6H_3NC$], 3.38 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H, ($Me_2C\underline{H})_2C_6H_3NC$], 6.83 [d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, $(Me_2CH)_2C_6\underline{H}_3NC$], 6.96 [m, 1H, $(Me_2CH)_2C_6\underline{H}_3NC$]. ^{1}H NMR ($CDCl_3$): 1.28 [d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, ($\underline{Me}_2CH)_2C_6H_3NC$], 3.41 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H, ($Me_2C\underline{H})_2C_6H_3NC$], 7.18 [d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, $(Me_2CH)_2C_6\underline{H}_3NC$], 7.32 [t, $^3J_{H\text{-}H}$ = 8 Hz, 1H, $(Me_2CH)_2C_6\underline{H}_3NC$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 22.2 [s, 4C, ($\underline{Me}_2CH)_2C_6H_3NC$], 29.5 [s, 2C, ($Me_2\underline{C}H)_2C_6H_3NC$], 122.9 [s, 2C, $(Me_2CH)_2\underline{C}_6H_3NC$], 124.0[m, 1C, $(Me_2CH)_2\underline{C}_6H_3NC$], 129.0 [s, 1C, $(Me_2CH)_2\underline{C}_6H_3NC$], 144.4 [s, 2C, $(Me_2CH)_2\underline{C}_6H_3NC$], 169.3 [s, 2C, $(Me_2CH)_2C_6H_3N\underline{C}$]. IR Data (ATR-IR neat liquid, cm^{-1}): 3072 (w), 3036 (w), 2965 (s), 2932 (m), 2873 (m), 2113 (vs) [ν(CN)], 1589 (w), 1462 (s), 1438 (m), 1386 (m), 1365 (m), 1351 (w), 1333 (w), 1261 (m), 1182 (m), 1165 (w), 1109 (m), 1063 (m), 1045 (m), 936 (m), 799 (s), 750 (vs), 678 (s), 659 (w), 556 (w), 424 (m). IR Data (CH_2Cl_2, cm^{-1}): ν_{CN} = 2118 (s).

Synthesis of 4-phenyl-2,6-diisopropylphenylisocyanide. A mixture of palladium(II) acetate (20 mg, 0.09 mmol), triphenylphosphine (40 mg, 0.15 mmol), cesium carbonate (2.50 g, 7.67 mmol), phenylboronic acid (355 mg, 2.91 mmol) and N-formyl-4-bromo-2,6-diisopropylaniline (750 mg, 2.64 mmol) was placed in an ampoule (500 mL) and treated with THF (80 mL) and then H_2O (5 mL). After the mixture was sparged with argon for *ca.* 10 minutes, the

ampoule was sealed and the mixture was heated to 85 °C with vigorous stirring for *ca.* 24 hours. The reaction was allowed to cool to room temperature, followed by the addition of H_2O (*ca.* 100 mL) and then Et_2O (*ca.* 100 mL). The layers were separated, and the organic layer was washed with saturated aqueous $NaHCO_3$ (*ca.* 100 mL). The organic layer was then dried with Na_2SO_4, filtered, and dried *in vacuo* to give N-formyl-4-phenyl-2,6-diisopropylaniline as an off-white solid of sufficient purity to be used directly for the synthesis of 4-phenyl-2,6-diisopropylphenylisocyanide as follows. All of the crude N-formyl-4-phenyl-2,6-diisopropylaniline was dissolved in CH_2Cl_2 (*ca.* 50 mL) and treated with diisopropylamine (1.33 mL, 9.49 mmol), which was then cooled to 0 °C using an ice-water bath. Phosphorus(V) oxychloride (500 μL, 5.36 mmol) was added dropwise over a period of 10 minutes. The mixture was allowed to warm to room temperature, and stirred for 3 hours. At this point, an aqueous solution of Na_2CO_3 (1.5 M, 50 mL, 75 mmol) was added, and the resulting biphasic mixture was allowed to stir overnight. The next morning the mixture was diluted with H_2O (*ca.* 50 mL) and then CH_2Cl_2 (*ca.* 100 mL), and the organic and aqueous layers were separated. The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 100 mL), dried with Na_2SO_4, filtered, and evaporated *in vacuo*. The resulting solid residue was dissolved in a minimal amount of CH_2Cl_2, placed on top of a CH_2Cl_2 saturated silica plug, and eluted with CH_2Cl_2 (CNdippPh detected in eluent by short-wave UV excitation). The eluent that contained CNdippPh was evaporated *in vacuo*. The resulting white solid was dissolved in a minimal amount of boiling hexanes, allowed to cool to room temperature and then placed into a –15 °C freezer to give large colorless crystals in two batches which were isolated and dried *in vacuo* giving 4-phenyl-2,6-diisopropylphenylisocyanide (CNdippPh, first batch – 340 mg, second batch – 50 mg, total - 390 mg, 56%). ^{1}H NMR ($CDCl_3$): 1.36 [d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, ($\underline{Me}_2CH)_2C_6H_2(C_6H_5)(NC)$], 3.45 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H, $(Me_2C\underline{H})_2C_6H_2(C_6H_5)(NC)$], 7.37 [s, 2H, $(Me_2CH)_2C_6\underline{H}_2(C_6H_5)(NC)$], 7.40 [tt, $^3J_{H\text{-}H}$ = 7 Hz, $^4J_{H\text{-}H}$ = 1 Hz, 1H, $(Me_2CH)_2C_6H_2(C_6\underline{H}_5)(NC)$], 7.48 [m, 2H, $(Me_2CH)_2C_6H_2(C_6\underline{H}_5)(NC)$], 7.58, [m, 2H, $(Me_2CH)_2C_6H_2(C_6\underline{H}_5)(NC)$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 22.8 [s, 4C, ($\underline{Me}_2CH)_2C_6H_2(C_6H_5)(NC)$], 30.1 [s, 2C, $(Me_2\underline{C}H)_2C_6H_2(C_6H_5)(NC)$], 122.4, [s, 2C, $(Me_2CH)_2\underline{C}_6H_2(C_6H_5)(NC)$], 123.6 [b, 1C, $(Me_2CH)_2\underline{C}_6H_2(C_6H_5)(NC)$], 127.4, [s, 2C, $(Me_2CH)_2C_6H_2(\underline{C}_6H_5)(NC)$], 128.0, [s, 1C, $(Me_2CH)_2C_6H_2(\underline{C}_6H_5)(NC)$], 129.0, [s, 2C, $(Me_2CH)_2C_6H_2(\underline{C}_6H_5)(NC)$], 140.7, [s, 1C, biaryl linker C], 142.4, [s, 1C, biaryl linker C], 145.5, [s, 2C, $(Me_2CH)_2\underline{C}_6H_2(C_6H_5)(NC)$], 169.1 [s, 1C, $(Me_2CH)_2C_6H_2(C_6H_5)(N\underline{C})$]. IR Data (ATR-IR drop casted from C_6H_6 solution, cm^{-1}): 3062 (w), 3032 (w), 2965 (s), 2930 (m), 2873 (m), 2111 (vs) [ν(CN)], 1598 (m), 1571 (w), 1494 (w), 1464 (s), 1448 (s), 1413 (m), 1386 (m), 1365 (m), 1346 (m), 1267 (w), 1250 (w), 1165 (w), 1136 (w), 1109 (w), 1075 (m), 1046 (w), 1027 (w), 961 (m), 945 (w), 918 (w), 883 (s), 823 (w), 762 (vs), 699 (vs), 634 (w), 609 (m), 434 (w). IR Data (CH_2Cl_2, cm^{-1}): ν_{CN} = 2119 (s).

Synthesis of 4-(4-biphenyl)-2,6-diisopropylphenylisocyanide. A mixture of palladium(II) acetate (20 mg, 0.09 mmol), triphenylphosphine (40 mg, 0.15 mmol), cesium carbonate (2.50 g, 7.67 mmol), 4-biphenylboronic acid (575 mg, 2.90 mmol) and N-formyl-4-bromo-2,6-diisopropylaniline (750 mg, 2.64 mmol) was placed in an ampoule (500 mL) and treated with THF (80 mL) and then H_2O (5 mL). After the mixture was sparged with argon for *ca.* 10 minutes, the ampoule was sealed and the mixture was heated to 85 °C with vigorous stirring for *ca.* 21 hours. The reaction was allowed to cool to room temperature, followed by the addition of H_2O (*ca.* 100 mL) and then Et_2O (*ca.* 100 mL). The layers were separated, and the organic layer was washed with saturated aqueous $NaHCO_3$ (*ca.* 100 mL). The organic layer was then dried with Na_2SO_4, filtered, and dried *in vacuo*. The resulting solid residue was dissolved in a minimal amount of

CH_2Cl_2, placed on top of a CH_2Cl_2 saturated silica plug, and eluted first with *ca.* 175 mL CH_2Cl_2, which was discarded, and then *ca.* 350 mL 80:20 CH_2Cl_2:MeOH, which contained N-formyl-4-(4-biphenyl)-2,6-diisopropylaniline. This eluent was evaporated *in vacuo* to give N-formyl-4-(4-biphenyl)-2,6-diisopropylaniline as an off-white solid of sufficient purity to be used directly for the synthesis of 4-(4-biphenyl)-2,6-diisopropylphenylisocyanide as follows. All of the crude N-formyl-4-(4-biphenyl)-2,6-diisopropylaniline was dissolved in CH_2Cl_2 (*ca.* 50 mL) and treated with diisopropylamine (1.33 mL, 9.49 mmol), which was then cooled to 0 °C using an ice-water bath. Phosphorus(V) oxychloride (350 μL, 3.76 mmol) was added dropwise over a period of 10 minutes. The mixture was allowed to warm to room temperature, and stirred for 3 hours. At this point, an aqueous solution of Na_2CO_3 (1.5 M, 30 mL, 45 mmol) was added, and the resulting biphasic mixture was allowed to stir overnight. The next morning the mixture was diluted with saturated aqueous $NaHCO_3$ (*ca.* 50 mL) and CH_2Cl_2 (*ca.* 50 mL), and the organic and aqueous layers were separated. The aqueous layer was extracted with additional CH_2Cl_2 (*ca.* 50 mL), and the combined organic extracts were dried with Na_2SO_4, filtered, and evaporated *in vacuo*. The resulting solid residue was dissolved in a minimal amount of CH_2Cl_2, placed on top of a CH_2Cl_2 saturated silica plug, and eluted with CH_2Cl_2 (CNdippPh^{Ph} detected in eluent by short-wave UV excitation). The eluent that contained CNdippPh^{Ph} was evaporated *in vacuo*. The resulting white solid was dissolved in a minimal amount of boiling hexanes, allowed to cool to room temperature and then placed into a –15 °C freezer to give large colorless crystals which were isolated and dried *in vacuo* giving 4-(4-biphenyl)-2,6-diisopropylphenylisocyanide (CNdippPh^{Ph}, 600 mg, 67%). ^{1}H NMR ($CDCl_3$): 1.37 [d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, ($\underline{Me}_2CH)_2C_6H_2(C_6H_5\text{-}C_6H_4)(NC)$], 3.46 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H, ($Me_2C\underline{H})_2C_6H_2(C_6H_5\text{-}C_6H_4)(NC)$], 7.39 [tt, $^3J_{H\text{-}H}$ = 7 Hz, $^4J_{H\text{-}H}$ = 1 Hz, 1H, $(Me_2CH)_2C_6H_2(C_6\underline{H}_5\text{-}C_6H_4)(NC)$], 7.42 [s, 2H, $(Me_2CH)_2C_6\underline{H}_2(C_6H_5\text{-}C_6H_4)(NC)$], 7.49 [m, 2H, $(Me_2CH)_2C_6H_2(C_6\underline{H}_5\text{-}C_6H_4)(NC)$], 7.65 [m, 4H, $(Me_2CH)_2C_6H_2(C_6\underline{H}_5\text{-}C_6\underline{H}_4)(NC)$], 7.71, [m, 2H, $(Me_2CH)_2C_6H_2(C_6H_5\text{-}C_6\underline{H}_4)(NC)$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 22.8 [s, 4C, ($\underline{Me}_2CH)_2C_6H_2(C_6H_5\text{-}C_6H_4)(NC)$], 30.1 [s, 2C, ($Me_2\underline{C}H)_2C_6H_2(C_6H_5\text{-}C_6H_4)(NC)$], 122.3, [s, 2C, $(Me_2CH)_2\underline{C}_6H_2(C_6H_5\text{-}C_6H_4)(NC)$], 123.6 [b, 1C, $(Me_2CH)_2\underline{C}_6H_2(C_6H_5\text{-}C_6H_4)(NC)$], 127.2 [s, 2C, $(Me_2CH)_2C_6H_2(C_6H_5\text{-}\underline{C}_6H_4)(NC)$], 127.7 [s, 1C, $(Me_2CH)_2C_6H_2(\underline{C}_6H_5\text{-}C_6H_4)(NC)$], 127.8 [s, 2C, $(Me_2CH)_2C_6H_2(C_6H_5\text{-}\underline{C}_6H_4)(NC)$], 127.8 [s, 2C, $(Me_2CH)_2C_6H_2(\underline{C}_6H_5\text{-}C_6H_4)(NC)$], 129.0, [s, 2C, $(Me_2CH)_2C_6H_2(\underline{C}_6H_5\text{-}C_6H_4)(NC)$], 139.6 [s, 1C, biaryl linker C], 140.6 [s, 1C, biaryl linker C], 141.0 [s, 1C, biaryl linker C], 141.9 [s, 1C, biaryl linker C], 145.6 [s, 2C, $(Me_2CH)_2\underline{C}_6H_2(C_6H_5\text{-}C_6H_4)(NC)$], 169.2 [s, 1C, $(Me_2CH)_2C_6H_2(_6H_5\text{-}C_6H_4)(N\underline{C})$]. IR Data (ATR-IR drop casted from C_6H_6 solution, cm^{-1}): 3060 (w), 3030 (w), 2965 (s), 2931 (m), 2873 (m), 2112 (vs) [ν(CN)], 1601 (m), 1579 (w), 1523 (w), 1488 (m), 1463 (m), 1398 (w), 1386 (w), 1365 (w), 1347 (w), 1268 (w), 1111 (w), 1076 (w), 1007 (w), 944 (w), 888 (w), 839 (s), 820 (w), 764 (vs), 731 (m), 697 (s), 555 (w), 504 (w). IR Data (CH_2Cl_2, cm^{-1}): ν_{CN} = 2118 (s).

Synthesis of 4-(3,5-dimethoxyphenyl)-2,6-diisopropylphenylisocyanide. A mixture of palladium(II) acetate (20 mg, 0.09 mmol), triphenylphosphine (60 mg, 0.23 mmol), cesium carbonate (4.00 g, 12.28 mmol), 3,5-dimethoxyphenylboronic acid (700 mg, 3.87 mmol) and N-formyl-4-bromo-2,6-diisopropylaniline (1.00 g, 3.52 mmol) was placed in an ampoule (500 mL) and treated with THF (80 mL) and then H_2O (6 mL). After the mixture was sparged with argon for *ca.* 20 minutes, the ampoule was sealed and the mixture was heated to 85 °C with vigorous stirring for *ca.* 20 hours. The reaction was allowed to cool to room temperature, followed by the addition of H_2O (*ca.* 100 mL) and then Et_2O (*ca.* 100 mL). The layers were separated, and the organic layer was washed with saturated aqueous $NaHCO_3$ (*ca.*

100 mL). The organic layer was then dried with Na_2SO_4, filtered, and dried *in vacuo* to give N-formyl-4-(3,5-dimethoxyphenyl)-2,6-diisopropylaniline of sufficient purity to be used directly for the synthesis of 4-(3,5-dimethoxyphenyl)-2,6-diisopropylphenylisocyanide as follows. All of the crude N-formyl-4-(3,5-dimethoxyphenyl)-2,6-diisopropylaniline was dissolved in CH_2Cl_2 (*ca.* 50 mL) and was treated with diisopropylamine (0.93 mL, 6.63 mmol), which was then cooled to 0 °C using an ice-water bath. Phosphorus(V) oxychloride (220 μL, 2.29 mmol) was added dropwise over a period of 10 minutes. The mixture was allowed to warm to room temperature, and stirred for 3 hours. At this point, an aqueous solution of Na_2CO_3 (1.5 M, 20 mL, 30 mmol) was added, and the resulting biphasic mixture was allowed to stir overnight. The next morning the mixture was diluted with H_2O (*ca.* 50 mL) and the CH_2Cl_2 (*ca.* 40 mL), and the organic and aqueous layers were separated, and the latter was extracted with CH_2Cl_2 (2 × *ca.* 50 mL). The combined organic extracts was dried with Na_2SO_4, filtered, and evaporated *in vacuo* to give 4-(3,5-dimethoxyphenyl)-2,6-diisopropylphenylisocyanide (CNdippPh^{OMe_2}, 586 mg, 52%) as an off-white solid. Colorless crystals of CNdippPh^{OMe_2} can be obtained by (*i*) slow evaporation of a saturated solution of CNdippPh^{OMe_2} in CH_2Cl_2 or (*ii*) dissolution of CNdippPh^{OMe_2} in a minimal amount of boiling hexanes, allowing the solution to cool to room temperature and then placing the solution into a −15 °C freezer. ^{1}H NMR ($CDCl_3$): 1.32 [d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, ($\underline{Me}_2CH)_2C_6H_2(C_6H_3OMe_2)(NC)$], 3.42 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H, ($Me_2C\underline{H})_2C_6H_2(C_6H_3OMe_2)(NC)$], 3.86 [s, 6H, ($Me_2CH)_2C_6H_2(C_6H_3O\underline{Me}_2)(NC)$], 6.50 [t, $^3J_{H\text{-}H}$ = 2 Hz, 1H, ($Me_2CH)_2C_6H_2(C_6\underline{H}_3OMe_2)(NC)$], 6.67 [d, $^3J_{H\text{-}H}$ = 2 Hz, 2H, ($Me_2CH)_2C_6H_2(C_6\underline{H}_3OMe_2)(NC)$], 7.32 [s, 2H, ($Me_2CH)_2C_6\underline{H}_2(C_6H_3OMe_2)(NC)$]. ^{13}C{^{1}H} NMR ($CDCl_3$): 22.8 [s, 4C, ($\underline{Me}_2CH)_2C_6H_2(C_6H_3OMe_2)(NC)$], 30.1 [s, 2C, ($Me_2\underline{C}H)_2C_6H_2(C_6H_3OMe_2)(NC)$], 55.6 [s, 2C, ($Me_2CH)_2C_6H_2(C_6H_3O\underline{Me}_2)(NC)$], 99.4 [s, 1C, ($Me_2CH)_2C_6H_2(\underline{C}_6H_3OMe_2)(NC)$], 106.0 [s, 2C, ($Me_2CH)_2C_6H_2(\underline{C}_6H_3OMe_2)(NC)$], 122.4 [s, 2C, ($Me_2CH)_2\underline{C}_6H_2(C_6H_3OMe_2)(NC)$], 123.8 [b, 1C, ($Me_2CH)_2\underline{C}_6H_2(C_6H_3OMe_2)(NC)$], 142.4 [s, 1C, biaryl linker C], 143.0 [s, 1C, biaryl linker C], 145.5 [s, 2C, ($Me_2CH)_2\underline{C}_6H_2(C_6H_3OMe_2)(NC)$], 161.3 [s, 2C, ($Me_2CH)_2C_6H_2(\underline{C}_6H_3OMe_2)(NC)$], 169.2 [s, 1C, ($Me_2CH)_2C_6H_2(C_6H_3OMe_2)(N\underline{C})$]. IR Data (ATR-IR drop casted from C_6H_6 solution, cm^{-1}): 3068 (w), 3003 (w), 2965 (s), 2927 (m), 2873 (w), 2840 (w), 2115 (s) [ν(CN)], 1605 (vs), 1591 (vs), 1573 (w), 1463 (m), 1442 (m), 1405 (m), 1352 (m), 1324 (m), 1257 (m), 1199 (s), 1163 (vs), 1107 (w), 1072 (m), 1043 (w), 991 (w), 947 (w), 925 (w), 905 (w), 878 (w), 836 (m), 819 (w), 775 (w), 764 (w), 698 (w), 675 (m), 576 (w), 460 (w), 407 (w). IR Data (CH_2Cl_2, cm^{-1}): ν_{CN} = 2119 (s).

Synthesis of 4-(3,4,5-trimethoxyphenyl)-2,6-diisopropylphenylisocyanide. A mixture of palladium(II) acetate (20 mg, 0.09 mmol), triphenylphosphine (40 mg, 0.15 mmol), cesium carbonate (2.50 g, 7.67 mmol), 3,4,5-trimethoxyphenylboronic acid (615 mg, 2.90 mmol) and N-formyl-4-bromo-2,6-diisopropylaniline (750 mg, 2.64 mmol) was placed in an ampoule (500 mL) and treated with THF (80 mL) and then H_2O (6 mL). The mixture was sparged with argon for *ca.* 10 minutes, at which point the ampoule was sealed, heated to 85 °C with vigorous stirring for *ca.* 24 hours. The reaction was allowed to cool to room temperature, followed by the addition of H_2O (*ca.* 100 mL) and then Et_2O (*ca.* 100 mL). The layers were separated, and the organic layer was washed with saturated aqueous $NaHCO_3$ (2 × *ca.* 100 mL). The organic layer was then dried with Na_2SO_4, filtered, and dried *in vacuo* to give N-formyl-4-(3,4,5-trimethoxyphenyl)-2,6-diisopropylaniline of sufficient purity to be used directly for the synthesis of 4-(3,4,5-dimethoxyphenyl)-2,6-diisopropylphenylisocyanide as follows. All of the crude N-formyl-4-(3,4,5-trimethoxyphenyl)-

2,6-diisopropylaniline was dissolved in CH_2Cl_2 (*ca.* 50 mL) and was treated with diisopropylamine (1.33 mL, 9.49 mmol), which was then cooled to 0 °C using an ice-water bath. Phosphorus(V) oxychloride (350 μL, 3.76 mmol) was added dropwise over a period of 10 minutes. The mixture was allowed to warm to room temperature, and stirred for 3 hours. At this point, the solution was cooled to 0 °C using an ice-water bath and an aqueous solution of Na_2CO_3 (1.5 M, 50 mL, 75 mmol) was added, and the resulting biphasic mixture was allowed to stir overnight. The next morning the mixture was diluted with saturated aqueous $NaHCO_3$ (*ca.* 100 mL) and then CH_2Cl_2 (*ca.* 100 mL), and the organic and aqueous layers were separated. The organic layer was washed with saturated aqueous $NaHCO_3$ (*ca.* 100 mL), dried with Na_2SO_4, filtered, and evaporated *in vacuo*. The resulting solid residue was dissolved in a minimal amount of CH_2Cl_2, placed on top of a CH_2Cl_2 saturated silica plug, and eluted with CH_2Cl_2 (CNdippPh^{OMe3} detected in eluent by short-wave UV excitation). The eluent that contained CNdippPh^{OMe3} was evaporated *in vacuo*. The resulting white solid was dissolved in a minimal amount of boiling hexanes, allowed to cool to room temperature and then placed into a –15 °C freezer to give large colorless crystals which were isolated and dried *in vacuo* giving 4-(3,4,5-dimethoxyphenyl)-2,6-diisopropylphenylisocyanide (CNdippPh^{OMe3}, 590 mg, 63%). ^{1}H NMR ($CDCl_3$): 1.34 [d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, $(\underline{Me}_2CH)_2C_6H_2(C_6H_2OMe_3)(NC)$], 3.43 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H, $(Me_2C\underline{H})_2C_6H_2(C_6H_2OMe_3)(NC)$], 3.90 [s, 3H, $(Me_2CH)_2C_6H_2(C_6H_2O\underline{Me}_3)(NC)$], 3.94 [s, 6H, $(Me_2CH)_2C_6H_2(C_6H_2O\underline{Me}_3)(NC)$], 6.71 [s, 2H, $(Me_2CH)_2C_6H_2(C_6\underline{H}_2OMe_3)(NC)$], 7.29 [s, 2H, $(Me_2CH)_2C_6\underline{H}_2(C_6H_2OMe_3)(NC)$]. ^{13}C{^{1}H} NMR ($CDCl_3$): 22.7 [s, 4C, $(\underline{Me}_2CH)_2C_6H_2(C_6H_2OMe_3)(NC)$], 30.1 [s, 2C, $(Me_2\underline{C}H)_2C_6H_2(C_6H_2OMe_3)(NC)$], 56.4 [s, 2C, $(Me_2CH)_2C_6H_2(C_6H_2O\underline{Me}_3)(NC)$], 61.1 [s, 1C, $(Me_2CH)_2C_6H_2(C_6H_2O\underline{Me}_3)(NC)$], 104.9 [s, 2C, $(Me_2CH)_2C_6H_2(\underline{C}_6H_2OMe_3)(NC)$], 122.3 [s, 2C, $(Me_2CH)_2\underline{C}_6H_2(C_6H_2OMe_3)(NC)$], 123.5 [b, 1C, $(Me_2CH)_2\underline{C}_6H_2(C_6H_2OMe_3)(NC)$], 136.8 [s, 1C, $(Me_2CH)_2C_6H_2(\underline{C}_6H_2OMe_3)(NC)$], 138.3 [s, 1C, biaryl linker C], 142.7 [s, 1C, biaryl linker C], 145.5 [s, 2C, $(Me_2CH)_2\underline{C}_6H_2(C_6H_2OMe_3)(NC)$], 153.6 [s, 2C, $(Me_2CH)_2C_6H_2(\underline{C}_6H_2OMe_3)(NC)$], 169.3 [s, 1C, $(Me_2CH)_2C_6H_2(C_6H_2OMe_3)(N\underline{C})$]. IR Data (ATR-IR drop casted from C_6H_6 solution, cm^{-1}): 3001 (w), 2960 (s), 2937 (m), 2872 (m), 2828 (w), 2115 (s) [ν(CN)], 1587 (s), 1572 (s), 1506 (s), 1462 (s), 1447 (s), 1428 (s), 1403 (w), 1380 (m), 1366 (s), 1358 (s), 1330 (w), 1270 (m), 1238 (vs), 1173 (m), 1129 (vs), 1069 (s), 1038 (m), 1004 (s), 956 (m), 943 (m), 918 (m), 891 (m), 877 (w), 849 (m), 833 (m), 818 (m), 802 (w), 764 (m), 740 (w), 677 (s), 669 (s), 590 (w), 528 (m), 500 (w), 468 (w). IR Data (CH_2Cl_2, cm^{-1}): ν_{CN} = 2118 (s).

Synthesis of W(CNdipp)$_6$. Sodium mercury amalgam, Na(Hg), was generated by adding small pieces of sodium (113 mg, 4.93 mmol) to mercury (*ca.* 10 g, 50 mmol). THF (*ca.* 25 mL), 2,6-diisopropylphenylisocyanide (500 mg, 2.67 mmol) and a suspension of $WCl_4(THF)_2$ (193 mg, 0.41 mmol) in THF (*ca.* 20 mL) was sequentially added to the amalgam. The resulting red mixture was stirred vigorously overnight. The next morning the mixture was evaporated to dryness *in vacuo* to give a dark-red residue. The leftover Na(Hg) was poured out of the reaction flask, and the residue in the flask was extracted into benzene twice (*ca.* 30 mL and then *ca.* 10 mL). The filtrate was concentrated to *ca.* one-third its volume while keeping the temperature of the solution at 40 °C. The red solution was allowed to stand giving red crystals that were dried *in vacuo* to give W(CNdipp)$_6$ (380 mg, 71%). ^{1}H NMR (C_6D_6): 1.27 [d, $^3J_{H\text{-}H}$ = 7 Hz, 72H, $\{(\underline{Me}_2CH)_2C_6H_3NC\}_6W$], 3.72 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 12H, $\{(Me_2C\underline{H})_2C_6H_3NC\}_6W$], 6.93 – 6.99 [m, 18H, $\{(Me_2CH)_2C_6\underline{H}_3NC\}_6W$]. ^{13}C{^{1}H} NMR ($C_6D_6$): 22.9 [s, 24C, $\{(\underline{Me}_2CH)_2C_6H_3NC\}_6W$], 30.5 [s, 12C,

{(Me$_2$CH)$_2$C$_6$H$_3$NC}$_6$W], 123.3 [s, 12C, {(Me$_2$CH)$_2$C$_6$H$_3$NC}$_6$W], 125.6 [s, 6C, {(Me$_2$CH)$_2$C$_6$H$_3$NC}$_6$W], 129.1 [s, 6C, {(Me$_2$CH)$_2$C$_6$H$_3$NC}$_6$W], 143.9 [s, 12C, {(Me$_2$CH)$_2$C$_6$H$_3$NC}$_6$W], 177.3 [s, 6C, {(Me$_2$CH)$_2$C$_6$H$_3$NC}$_6$W]. IR Data (ATR-IR drop casted from C_6H_6 solution, cm^{-1}): 3062 (w), 2961 (m), 2928 (w), 2867 (w), 1938 (vs) [ν(CN)], 1582 (m), 1460 (w), 1431 (m), 1383 (w), 1362 (w), 1330 (w), 1249 (w), 1182 (w), 808 (w), 793 (m), 748 (m), 665 (w), 500 (m), 470 (w).

Synthesis of W(CNdippPh)$_6$. Sodium mercury amalgam, Na(Hg) was generated by adding small pieces of sodium (20 mg, 0.9 mmol) to mercury (*ca.* 2.6 g, 13 mmol). To the amalgam was added a solution of CNdippPh (60 mg, 0.23 mmol) in THF (*ca.* 2 mL), followed by a suspension of $WCl_4(THF)_2$ (17 mg, 0.04 mmol) in THF (*ca.* 2 mL), followed by additional THF (*ca.* 2 mL). The resulting red mixture was stirred vigorously overnight. The next morning the mixture was evaporated to dryness *in vacuo* to give a dark-red residue, which was extracted into hot (50 °C) benzene (6 × *ca.* 1 mL). Pentane was allowed to vapor diffuse into the room temperature benzene solution, giving red crystals in two batches, that were washed with pentane (*ca.* 1 mL) and dried *in vacuo* to give W(CNdippPh)$_6$ (first batch – 36 mg, second batch – 4 mg, total – 40 mg, 65%). ^{1}H NMR (C_6D_6): 1.43 [d, $^3J_{H\text{-}H}$ = 7 Hz, 72H, {(Me$_2$CH)$_2$C$_6$H$_2$(C$_6$H$_5$)(NC)}$_6$W], 3.88 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 12H, {(Me$_2$CH)$_2$C$_6$H$_2$(C$_6$H$_5$)(NC)}$_6$W], 7.13 [tt, $^3J_{H\text{-}H}$ = 7 Hz, $^4J_{H\text{-}H}$ = 1 Hz, 6H, {(Me$_2$CH)$_2$C$_6$H$_2$(C$_6$H$_5$)(NC)}$_6$W], 7.22 [m, 12H, {(Me$_2$CH)$_2$C$_6$H$_2$(C$_6$H$_5$)(NC)}$_6$W], 7.46 [s, 12H, {(Me$_2$CH)$_2$C$_6$H$_2$(C$_6$H$_5$)(NC)}$_6$W], 7.53, [m, 12H, {(Me$_2$CH)$_2$C$_6$H$_2$(C$_6$H$_5$)(NC)}$_6$W]. ^{13}C{^{1}H} NMR (C_6D_6): 23.0 [s, 24C, {(Me$_2$CH)$_2$C$_6$H$_2$(C$_6$H$_5$)(NC)}$_6$W], 30.9 [s, 12C, {(Me$_2$CH)$_2$C$_6$H$_2$(C$_6$H$_5$)(NC)}$_6$W], 122.5, [s, 12C, {(Me$_2$CH)$_2$C$_6$H$_2$(C$_6$H$_5$)(NC)}$_6$W], 127.3 [s, 6C of Ar], 127.5 [s, 12C of Ar], 128.6 [b, 6C, {(Me$_2$CH)$_2$C$_6$H$_2$(C$_6$H$_5$)(NC)}$_6$W], 129.0 [s, 12C of Ar], 138.8 [s, 6C of Ar], 141.9 [s, 6C of Ar], 144.5 [s, 12C of Ar], 177.6 [s, 6C, {(Me$_2$CH)$_2$C$_6$H$_2$(C$_6$H$_5$)(NC)}$_6$W]. IR Data (ATR-IR drop casted from C_6H_6 solution, cm^{-1}): 3060 (w), 3031 (w), 2960 (m), 2928 (w), 2869 (w), 1948 (vs) [ν(CN)], 1598 (m), 1452 (m), 1440 (m), 1414 (m), 1384 (w), 1363 (w), 1328 (w), 1301 (w), 1254 (w), 1173 (w), 1076 (w), 1026 (w), 882 (m), 852 (w), 760 (m), 736 (m), 696 (m), 676 (w), 522 (m), 476 (w).

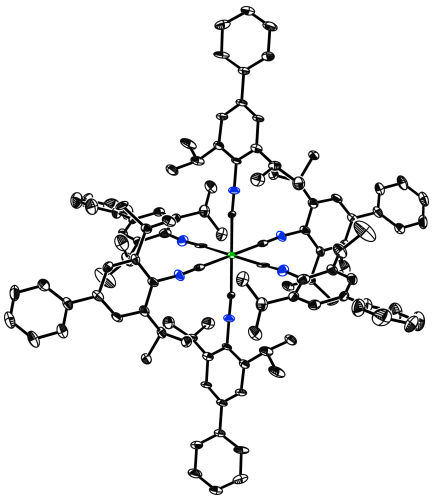

Figure S1. ***Molecular structure of W(CNdippPh)$_6$ (Green atom = W; blue atoms = N; black atoms = C).***

Synthesis of W(CNdippPh^{Ph})$_6$. Sodium mercury amalgam, Na(Hg), was generated by adding small pieces of sodium (33 mg, 1.4 mmol) to mercury (*ca.* 4.4 g, 22 mmol). To the amalgam was added a solution of CNdippPh^{Ph} (142 mg, 0.42 mmol) in THF (*ca.* 2 mL), followed by a suspension of $WCl_4(THF)_2$ (30 mg, 0.06 mmol) in THF (*ca.* 2 mL), followed by additional THF (*ca.* 2 mL). The resulting red mixture was stirred vigorously overnight. The next afternoon the mixture was evaporated to dryness *in vacuo* to give a dark-red residue, which was extracted into benzene (6 × *ca.* 1 mL). Pentane was allowed to vapor diffuse into the benzene solution, giving red crystals, which were dissolved in C_6H_6 (*ca.* 5 mL), filtered and lyophilized to give W(CNdippPh^{Ph})$_6$ (116 mg, 82%). ^{1}H NMR (C_6D_6): 1.53 [d, $^3J_{H\text{-}H}$ = 7 Hz, 72H, {($\underline{Me}_2CH)_2C_6H_2(C_6H_5\text{-}C_6H_4)(NC)\}_6W$], 3.97 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 12H, {$(Me_2C\underline{H})_2C_6H_2(C_6H_5\text{-}C_6H_4)(NC\}_6W$], 7.17 [m, 12H of Ar], 7.27 [m, 12H of Ar], 7.55 [m, 18H of Ar], 7.57 [s, 12H, {$(Me_2CH)_2C_6\underline{H}_2(C_6H_5\text{-}C_6H_4)(NC\}_6W$], 7.63, [m, 12H of Ar]. ^{13}C{^{1}H} NMR (C_6D_6): 23.1 [s, 24C, {($\underline{Me}_2CH)_2C_6H_2(C_6H_5\text{-}C_6H_4)(NC)\}_6W$], 31.0 [s, 12C, {$(Me_2\underline{C}H)_2C_6H_2(C_6H_5\text{-}C_6H_4)(NC)\}_6W$], 122.5, [s, 12C, {$(Me_2CH)_2\underline{C}_6H_2(C_6H_5\text{-}C_6H_4)(NC)\}_6W$], 127.4 [s, 12C of Ar], 127.6 [s, 12C of Ar], 128.0 [s, 12C of Ar], 128.4 [s, 6C of Ar], 128.6 [s, 6C, {$(Me_2CH)_2\underline{C}_6H_2(C_6H_5\text{-}C_6H_4)(NC)\}_6W$], 129.2 [s, 12C of Ar], 138.4 [s, 6C of Ar], 140.5 [s, 6C of Ar], 140.8 [s, 6C of Ar], 141.3 [s, 6C of Ar], 144.7 [s, 12C of Ar], 177.6 [s, 6C, {$(Me_2CH)_2C_6H_2(_6H_5\text{-}C_6H_4)(N\underline{C})\}_6W$]. IR Data (ATR-IR drop casted from C_6H_6 solution, cm^{-1}): 3059 (w), 3027 (w), 2961 (m), 2929 (w), 2870 (w), 1940 (vs) [ν(CN)], 1598 (m), 1487 (w), 1453 (m), 1440 (m), 1384 (w), 1363 (w), 1346 (w), 1302 (m), 1007 (w), 887 (w), 837 (m), 763 (m), 731 (m), 716 (w), 697 (m), 677 (w), 524 (m).

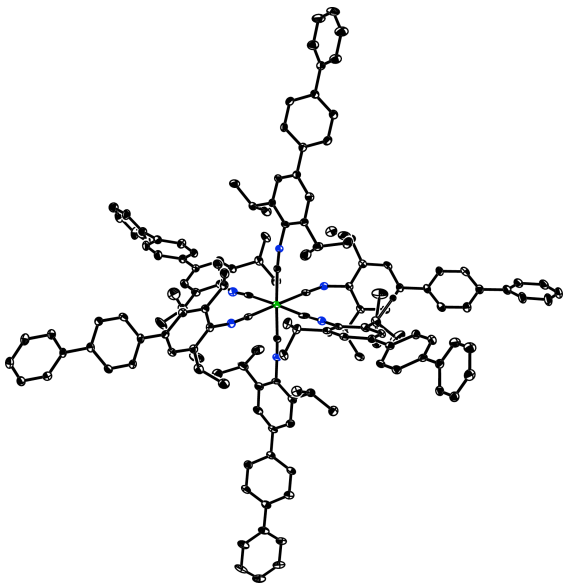

Figure S2. ***Molecular structure of W(CNdippPh^{Ph})$_6$ (Green atom = W; blue atoms = N; black atoms = C).***

Synthesis of W(CNdippPh^{OMe2})$_6$. Sodium mercury amalgam, Na(Hg), was generated by adding small pieces of sodium (31 mg, 1.4 mmol) to mercury (*ca.* 4.7 g, 23 mmol). To the amalgam was added a solution of CNdippPh^{OMe2} (122 mg, 0.38 mmol) in THF (*ca.* 2 mL), followed by a suspension of $WCl_4(THF)_2$ (27 mg, 0.06 mmol) in THF (*ca.* 2 mL), followed by additional THF (*ca.* 2 mL). The resulting red mixture was stirred vigorously overnight. The next morning the

mixture was evaporated to dryness *in vacuo* to give a dark- red residue, which was extracted into benzene (6 × *ca.* 1 mL). Pentane was allowed to vapor diffuse into the benzene solution, giving red crystals that were dried *in vacuo* to give $W(CNdippPh^{OMe_2})_6$ (106 mg, 87%). ^1H NMR (C_6D_6): 1.40 [d, $^3J_{H\text{-}H}$ = 7 Hz, 72H, $\{(\underline{Me}_2CH)_2C_6H_2(C_6H_3OMe_2)(NC)\}_6W$], 3.35 [s, 36H, $\{(Me_2CH)_2C_6H_2(C_6H_3O\underline{Me}_2)(NC)\}_6W$], 3.85 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 12H, $\{(Me_2C\underline{H})_2C_6H_2(C_6H_3OMe_2)(NC)\}_6W$], 6.57 [t, $^3J_{H\text{-}H}$ = 2 Hz, 6H, $\{(Me_2CH)_2C_6H_2(C_6\underline{H}_3OMe_2)(NC)\}_6W$], 6.93 [d, $^3J_{H\text{-}H}$ = 2 Hz, 12H, $\{(Me_2CH)_2C_6H_2(C_6\underline{H}_3OMe_2)(NC)\}_6W$], 7.52 [s, 12H, $\{(Me_2CH)_2C_6\underline{H}_2(C_6H_3OMe_2)(NC)\}_6W$]. $^{13}C\{^1H\}$ NMR (C_6D_6): 23.0 [s, 24C, $\{(\underline{Me}_2CH)_2C_6H_2(C_6H_3OMe_2)(NC)\}_6W$], 30.9 [s, 12C, $\{(Me_2\underline{C}H)_2C_6H_2(C_6H_3OMe_2)(NC)\}_6W$], 55.0 [s, 12C, $\{(Me_2CH)_2C_6H_2(C_6H_3O\underline{Me}_2)(NC)\}_6W$], 99.7 [s, 6C of Ar], 106.3 [s, 12C of Ar], 122.7 [s, 12C of Ar], 128.5 [s, 6C of Ar], 139.1 [s, 6C of Ar], 144.4 [s, 6C of Ar], 144.6 [s, 12C of Ar], 161.9 [s, 12C of Ar], 177.7 [s, 6C, $\{(Me_2CH)_2C_6H_2(C_6H_3OMe_2)(N\underline{C})\}_6W$]. IR Data (ATR-IR drop casted from C_6H_6 solution, cm^{-1}): 2959 (m), 2931 (w), 2871 (w), 2836 (w), 1949 (vs) [ν(CN)], 1594 (m), 1458 (m), 1433 (m), 1404 (w), 1358 (w), 1264 (m), 1202 (m), 1174 (w), 1154 (m), 1066 (w), 1042 (w), 843 (w), 832 (w), 790 (m), 760 (w), 695 (m), 678 (w), 527 (m), 459 (w).

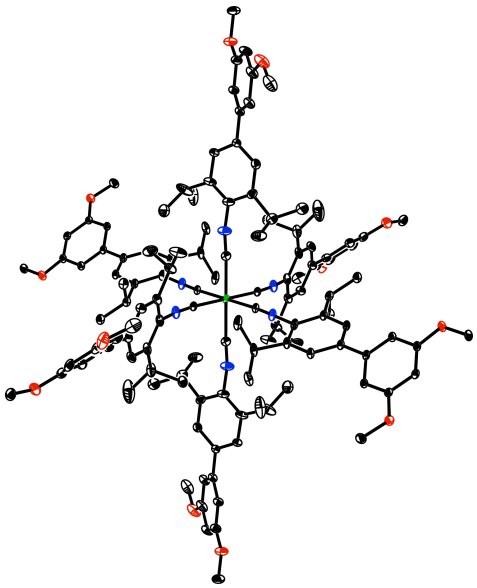

Figure S3. ***Molecular structure of $W(CNdippPh^{OMe_2})_6$ (Green atom = W; blue atoms = N; red atoms = O; black atoms = C).***

Synthesis of $W(CNdippPh^{OMe_3})_6$. Sodium mercury amalgam, Na(Hg), was generated by adding small pieces of sodium (20 mg, 0.9 mmol) to mercury (*ca.* 6.0 g, 30 mmol). A solution of $CNdippPh^{OMe_3}$ (76 mg, 0.21 mmol) in THF (*ca.* 3 mL) was added to the amalgam, followed by a suspension of $WCl_4(THF)_2$ (16 mg, 0.03 mmol) in THF (*ca.* 2 mL) and additionally THF (*ca.* 2 mL). The resulting red mixture was stirred vigorously overnight. The next morning the mixture was evaporated to dryness *in vacuo* to give a dark-red residue, which was extracted into benzene (3 × *ca.* 3 mL). Pentane was allowed to vapor diffuse into the benzene solution, giving red crystals that were washed with pentane (2 × *ca.* 3 mL) and dried *in vacuo* to give $W(CNdippPh^{OMe_3})_6$ (54 mg, 71%). ^1H NMR (C_6D_6): 1.54 [d, $^3J_{H\text{-}H}$ = 7 Hz, 72H, $\{(MeO)_3C_6H_2(\underline{Me}_2CH)_2C_6H_2NC\}_6W$], 3.39 [s, 36H, $\{(\underline{Me}O)_3C_6H_2(Me_2CH)_2C_6H_2NC\}_6W$], 3.89 [s, 18H,

{(MeO)$_3$C$_6$H$_2$(Me$_2$CH)$_2$C$_6$H$_2$NC}$_6$W], 3.98 [sept, $^3J_{H\text{-}H}$ = 7 Hz, 12H, {(MeO)$_3$C$_6$H$_2$(Me$_2$CH)$_2$C$_6$H$_2$NC}$_6$W], 6.79 [s, 12H, {(MeO)$_3$C$_6$H$_2$(Me$_2$CH)$_2$C$_6$H$_2$NC}$_6$W], 7.53 [s, 12H, {(MeO)$_3$C$_6$H$_2$(Me$_2$CH)$_2$C$_6$H$_2$NC}$_6$W]. ^{13}C{^{1}H} NMR (C_6D_6): 23.0 [s, 12C, {(MeO)$_3$C$_6$H$_2$(Me$_2$CH)$_2$C$_6$H$_2$NC}$_6$W], 31.1 [s, 6C, {(MeO)$_3$C$_6$H$_2$(Me$_2$CH)$_2$C$_6$H$_2$NC}$_6$W], 56.0 [s, 12C, {(MeO)$_3$C$_6$H$_2$(Me$_2$CH)$_2$C$_6$H$_2$NC}$_6$W], 60.6 [s, 6C, {(MeO)$_3$C$_6$H$_2$(Me$_2$CH)$_2$C$_6$H$_2$NC}$_6$W], 106.0 [s, 12C of Ar], 122.7 [s, 12C of Ar], 128.6 [s, 6C of Ar], 137.7 [s, 6C of Ar], 139.5 [s, 6C of Ar], 139.7 [s, 6C of Ar], 144.5 [s, 12C of Ar], 154.5 [s, 12C of Ar], 177.5 [s, 6C, {(MeO)$_3$C$_6$H$_2$(Me$_2$CH)$_2$C$_6$H$_2$NC}$_6$W]. IR Data (ATR-IR drop casted from C_6H_6 solution, cm^{-1}): 2960 (m), 2934 (m), 2831 (w), 1942 (vs) [ν(CN)], 1585 (m), 1504 (m), 1458 (m), 1440 (m), 1430 (m), 1399 (m), 1357 (w), 1270 (m), 1235 (m), 1183 (w), 1126 (s), 1068 (w), 1007 (m), 956 (w), 888 (w), 833 (m), 808 (m), 770 (m), 741 (w), 678 (m), 525 (m), 458 (w).

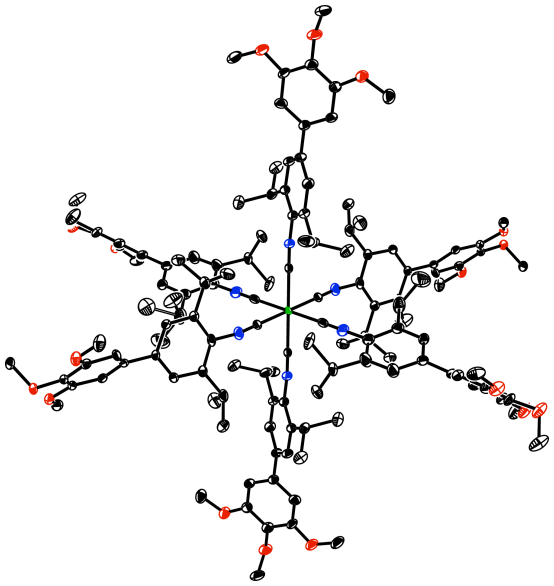

Figure S4. ***Molecular structure of W(CNdippPh^{OMe_3})$_6$ (Green atom = W; blue atoms = N; red atoms = O; black atoms = C).***

Table S1. Crystal, intensity collection, and refinement data.

	$W(CNdippPh)_6$	$W(CNdippPh^{Ph})_6$[a]	$W(CNdippPh^{OMe2})_6$[b]	$W(CNdippPh^{OMe3})_6$
lattice	Triclinic	Monoclinic	Triclinic	Monoclinic
formula	$C_{114}H_{126}N_6W$	$C_{161}H_{168}N_6W$	$C_{150}H_{174}N_6O_{12}W$	$C_{132}H_{162}N_6O_{18}W$
formula weight	1764.05	2370.85	2436.80	2304.52
space group	P–1	C2/c	P–1	$P2_1/c$
a/Å	14.456(3)	44.228(10)	13.4059(5)	13.6451(10)
b/Å	18.045(3)	13.454(3)	17.0452(6)	20.7417(11)
c/Å	18.803(4)	46.847(10)	17.3447(6)	21.9870(16)
a/°	85.655(6)	90	62.0827(14)	90
b/°	87.973(6)	111.074(3)	82.6020(16)	91.886(2)
c/°	81.028(5)	90	70.1845(15)	90
V/Å^3	4829.6(15)	26012(10)	3292.6(2)	6219.4(7)
Z	2	8	1	2
temperature (K)	100	100	100	100
radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073
ρ(calcd.), g cm^{-3}	1.213	1.211	1.229	1.231
μ(Mo Kα), mm^{-1}	1.247	0.943	0.940	0.994
θ max, deg.	32.438	29.170	30.508	33.971
no. of data collected	30730	32718	19678	25166
no. of data used	17249	21032	18992	11195
no. of parameters	1170	1577	781	766
R_1 [$I > 2\sigma(I)$]	0.0776	0.0804	0.0464	0.0747
wR_2 [$I > 2\sigma(I)$]	0.1152	0.1411	0.1128	0.1263
R_1 [all data]	0.1583	0.1430	0.0507	0.1964
wR_2 [all data]	0.1283	0.1609	0.1173	0.1597
GOF	1.350	1.105	1.086	1.016

(a) Crystallized with one molecule of benzene and one molecule of pentane in the unit cell. (b) Crystallized with four molecules of benzene in the unit cell.

Extinction coefficient measurments. An Ocean Optics 2000+ spectrophotometer using fiber optics to transport the light to and from a cuvette holder in a nitrogen filled glovebox was used for extinction coefficient measurements. The spectrometer was controlled with the Ocean Optics SpectraSuite software package. Stock solutions of **1** – **5** were made in toluene. A 10 μL microsyringe was used to add volumes of these stock solutions to 2 mL of either toluene, THF or MeCN in a cuvette (the pure solvent was used as the background). Absorption spectra were taken at multiple concentrations. A plot of concentration vs. absorbance at a specific wavelength were fit to a linear equation; the extinction coefficients as the slope of the line.

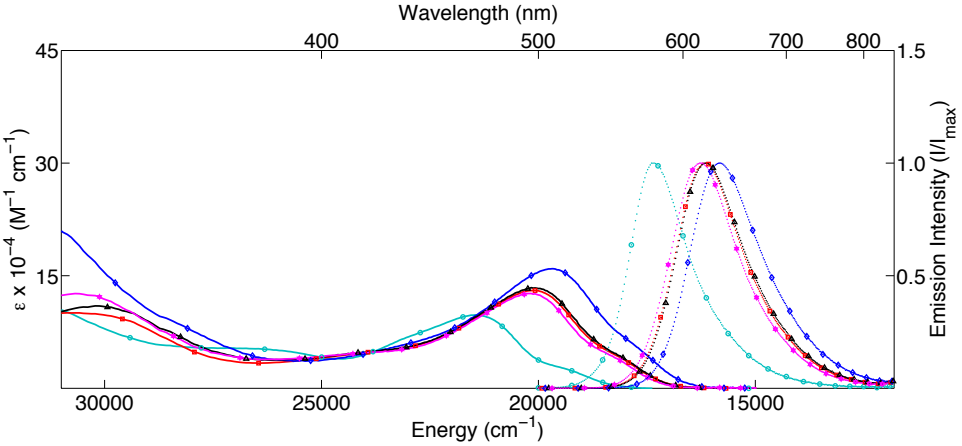

Figure S5. Absorption (solid lines) and emission (dotted lines) spectra of $W(CNdipp)_6$ (cyan/circle), $W(CNdippPh)_6$ (red/square), $W(CNdippPh^{Ph})_6$ (blue/diamond), $W(CNdippPh^{OMe_2})_6$ (black/triangle) and $W(CNdippPh^{OMe_3})_6$ (maroon/hexagram) in toluene solutions.

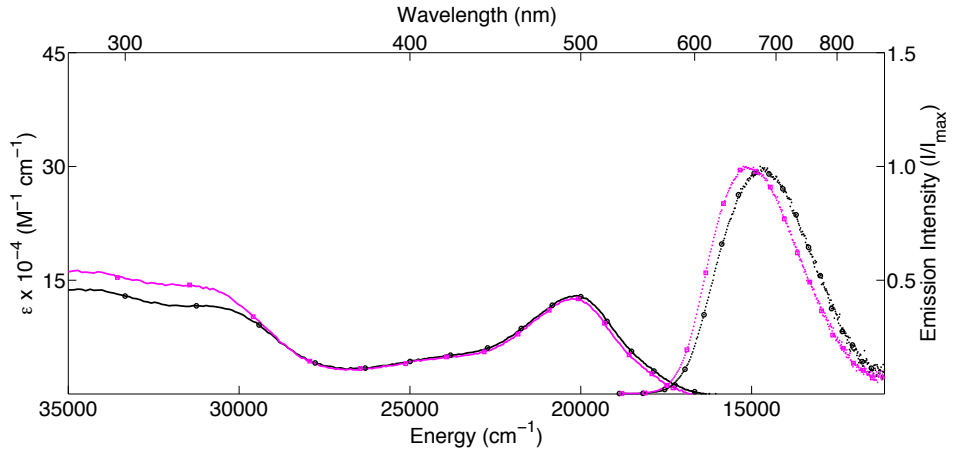

Figure S6. Absorption (solid lines) and emission (dotted lines) spectra of $W(CNdippPh^{OMe_2})_6$ (black/triangle) and $W(CNdippPh^{OMe_3})_6$ (maroon/hexagram) in MeCN solutions.

Excitation spectra. Excitation spectra were measured under optically dilute conditions in THF solutions. Emission observed at λ_{max}.

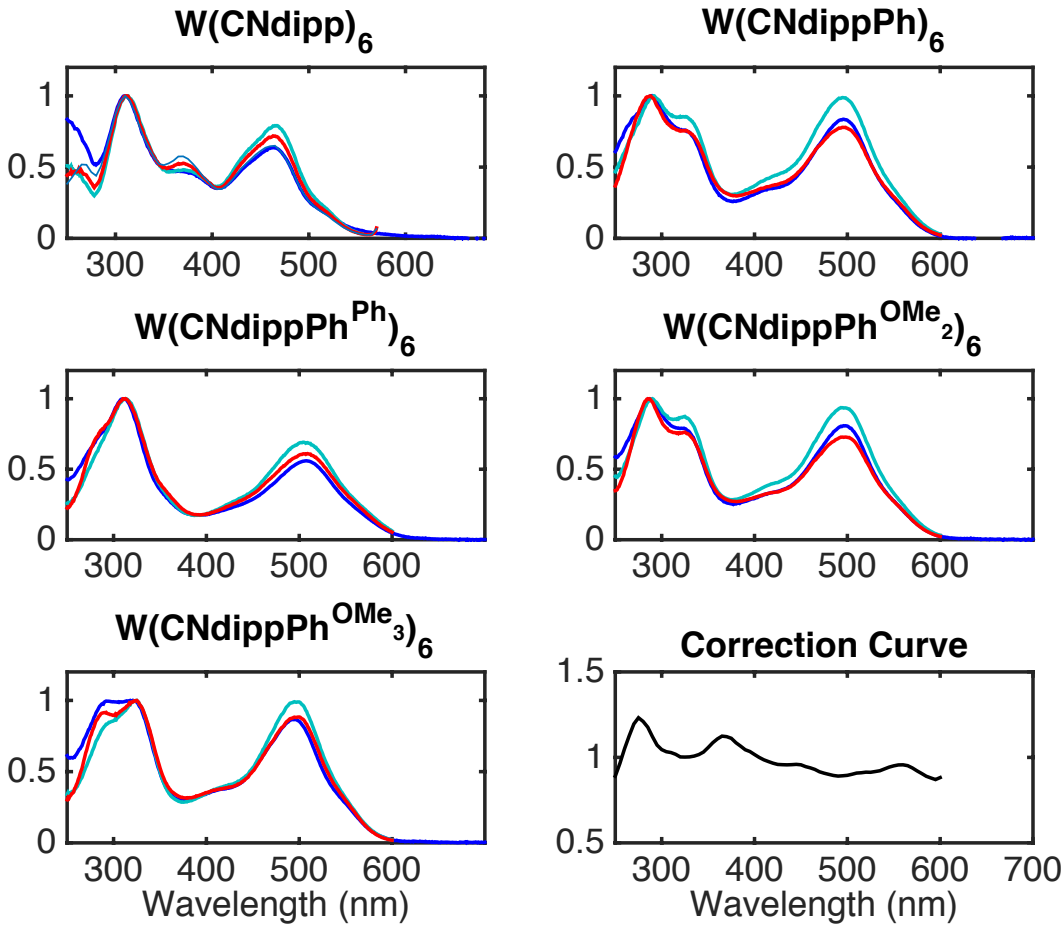

Figure S7. Corrected normalized excitation spectra (cyan, correction curve (black) supplied by the manufacturer shown in lower right plot), uncorrected normalized excitation spectra (red) and normalized absorption spectra (blue) in THF solutions.

Quantum yield Measurements. Quantum yields (ϕ_{PL}) were measured under optically dilute conditions by comparison to $[Ru(bpy)_3][PF_6]_2$ in MeCN ($\phi_{PL} = 0.062$),[1,2] according to the equation:

$$\phi_X = \phi_R \cdot \frac{A_R}{A_X} \cdot \frac{I_X}{I_R} \cdot \frac{\eta_x^2}{\eta_R^2},$$

where A_X and A_R are the absorbance's at the exciting wavelength (450 nm for all measurements), I_X and I_R are the integrated emission intensities, η_x^2 and η_R^2 are the squares of the refractive indices of the solvents used. Subscripts X and R refer to the unknown (*i.e.*, $W(CNAr)_6$ complexes) and reference solutions, respectively.

Absorption spectra were collected before and after emission spectra were taken; quantum yields were calculated for both A_{450} values to make sure there was no significant change.

77K excited state decay measurements. Measurements were made at 77K by immersing NMR tubes equipped with J. Young valves containing $W(CNAr)_6$ complexes in either toluene or 2-MeTHF in a glass dewar filled with liquid nitrogen.

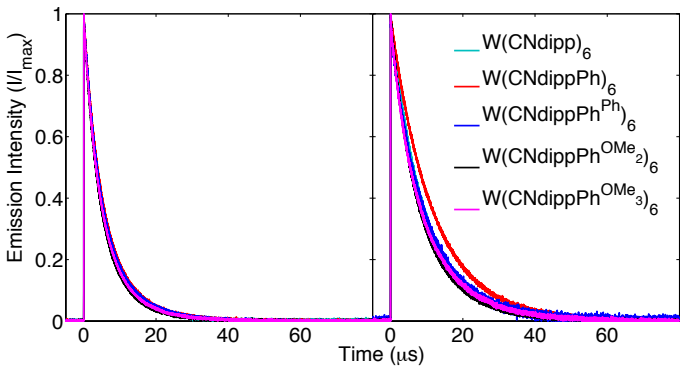

Figure S8. Time-resolved luminescence traces for $W(CNAr)_6$ complexes in toluene (left) and 2-MeTHF (right) glasses at 77 K (λ_{ex} = 488 nm, 8 ns pulse).

Table S2. Mean lifetime values (μs) for W(CNAr)6 complexes at 77 K.

$W(CNAr)_6$	Toluene	2-MeTHF
$W(CNdipp)_6$	5.6	9.1
$W(CNdippPh)_6$	6.1	10.9
$W(CNdippPh^{Ph})_6$	5.2	8.3
$W(CNdippPh^{OMe_2})_6$	5.3	8.2
$W(CNdippPh^{OMe_3})_6$	5.6	9.1

77K steady-state emission measurements. Measurements were made at 77K by immersing NMR tubes equipped with J. Young valves containing $W(CNAr)_6$ complexes in either toluene or 2-MeTHF in a glass dewar filled with liquid nitrogen. An optical fiber was used to transport the light emitted from the sample to a Melles Griot CCD detector.

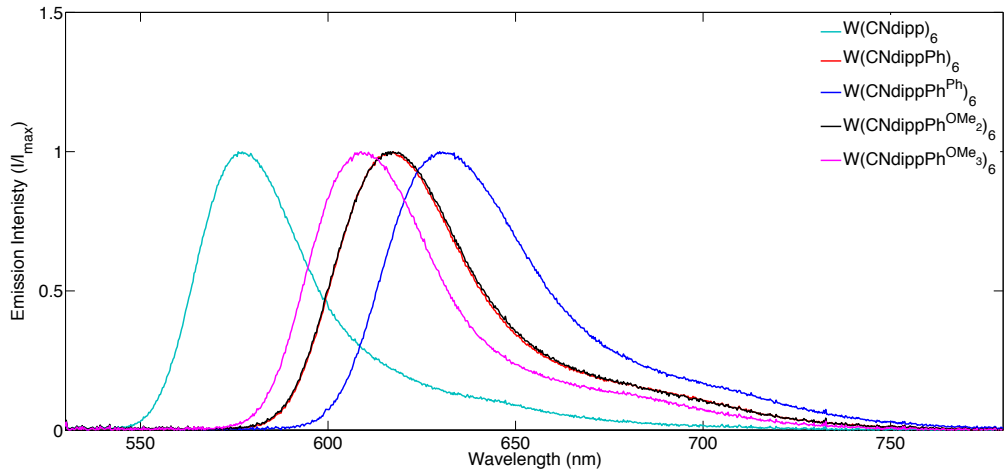

Figure S9. Steady-state emission spectra for $W(CNAr)_6$ complexes in toluene glasses at 77 K (λ_{ex} = 488 nm).

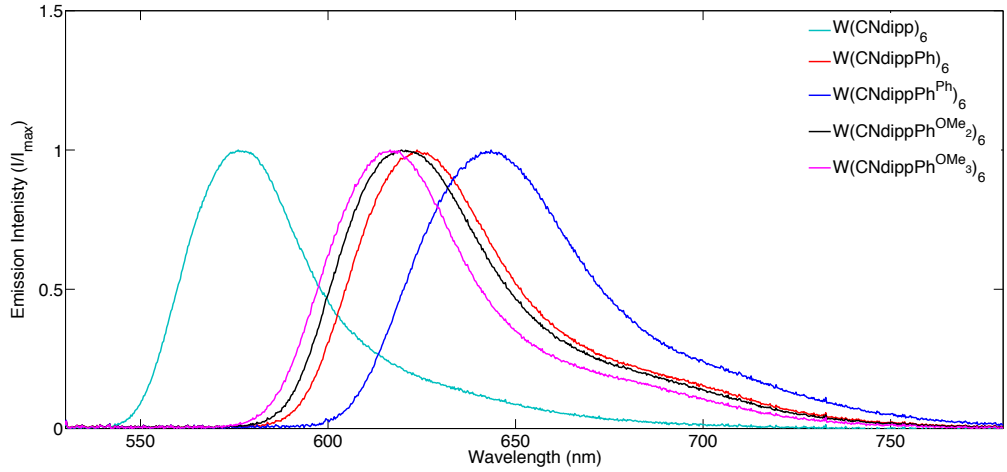

Figure S10. Steady-state emission spectra for $W(CNAr)_6$ complexes in 2-MeTHF glasses at 77 K (λ_{ex} = 488 nm).

Ligand Field (LF) Analysis. In order to determine if LF states (assuming O_h symmetry) are accessible for thermal activation from the MLCT excited state ($^3T_{1u}$), the harmonic potential surfaces of the $^1T_{1g}$, $^1T_{2g}$, $^3T_{2g}$ and $^5T_{2g}$ LF states of $W(CNAr)_6$ were estimated from spectroscopic data on $W(CO)_6$,[3] as the ligand field strength of ArNC is comparable to CO.[4] This type of analysis was completed for $[Co(OH_2)_6]^{3+}$, borrowing data from $[Co(NH_3)_6]^{3+}$,[5] in order to determine the activation energy for thermal crossing from the ground state into the $^5T_{2g}$ LF state.[6]

In $W(CO)_6$, the vertical transition energies, *i.e.*, the Franck-Condon energies, E_{FC}, from the ground state ($^1A_{1g}$) to the $^1T_{1g}$, $^1T_{2g}$ and $^3T_{2g}$ states are 29,950, 37,100 and 28,300 cm^{-1}, respectively (these data are taken from Gray and Beach, Ref. 3; DFT calculations[7] suggest that the ligand field states are substantially higher, which means that our estimates of activation barriers are lower limits). From these data,[3] the Racah parameters (B and C) and Dq, can be determined to be 447, 825 and 3,078 cm^{-1}, respectively. Therefore, E_{FC} for the $^5T_{2g}$ state is:: $E_{FC}(^5T_{2g} \leftarrow {}^1A_{1g}) = 20Dq - 5B - 8C$, giving ~ 52,700 cm^{-1}. In order to calculate minima of the potential surfaces, E_0, ($E_0 = E_{FC}$

– λ and λ = $\hbar\omega S_{a_{1g}}$), Huang-Rhys parameter (S, 2.4 for the $^3T_{2g}$ state and 9.6 for the $^5T_{2g}$ state) and metal ligand stretching frequency ($\hbar\omega$, 473 cm^{-1}),[8] values have been taken from previous work.

Based on our analysis, the lowest energy LF state is $^3T_{1g}$, estimated to be ~ 27,000 cm^{-1} above the ground state. As emission occurs from a MLCT excited state with an E_0 of ~ 18,300 cm^{-1}, a *lower* estimate (assuming same distortion coordinate) of the activation energy required to reach a LF state is > 8,500 cm^{-1}, which is much too large to account for the excited state decay kinetics observed.

Stern-Volmer analyses for reactions of *W(CNdipp)$_6$ and *W(CNdippPh^{OMe2})$_6$ with benzophenone and acetophenone.

Benzophenone quenching of *W(CNdippPh^{OMe2})$_6$ in THF.

Benzophenone (39.0 mg, 0.21 mmol) was dissolved in THF (4 mL) to give a 53.5 mM solution. 1.5 mL of a stock solution of W(CNdippPh^{OMe2})$_6$ (< 5 μM) in THF was added to five separate cuvettes. 0, 10, 20, 30 and 40 μL of the 53.5 mM benzophenone solution were added to the five cuvettes, giving final concentrations of 0, 0.35, 0.70, 1.05 and 1.39 mM benzophenone, respectively. Excited state lifetimes were then determined for each sample.

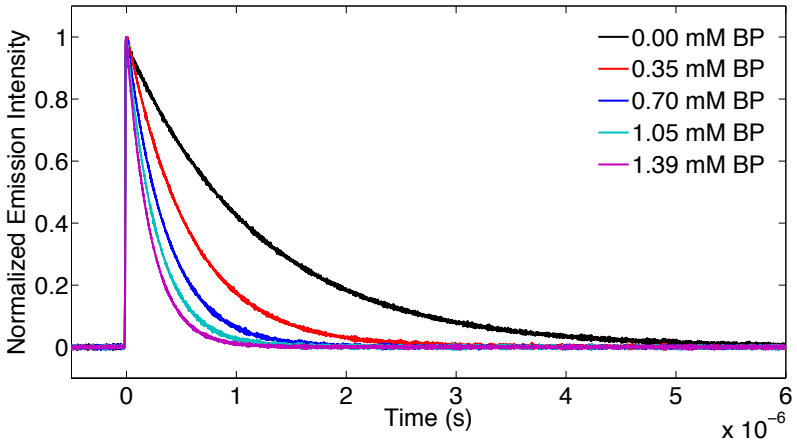

Figure S11. Quenching of *W(CNdippPh^{OMe2})$_6$ with different concentrations of benzophenone. Wes-2-108

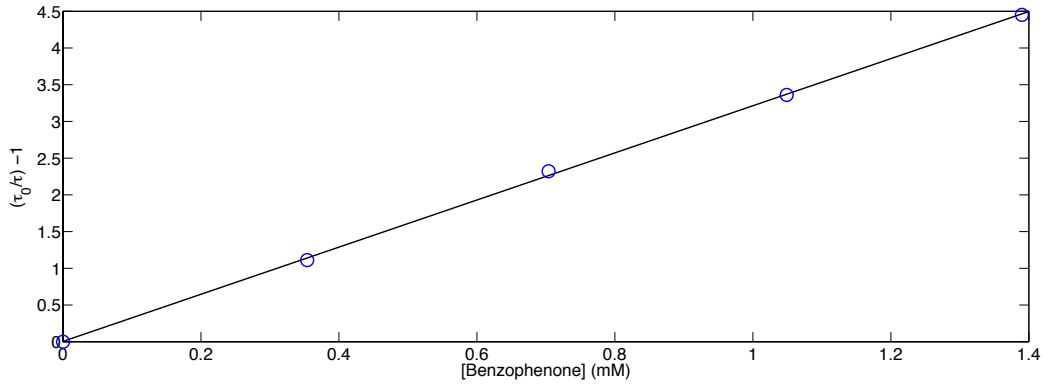

Figure S12. Plot of benzophenone concentration (mM) vs. $(\tau_0/\tau) - 1$ for W(CNdippPh^{OMe2})$_6$ to give a quenching rate constant of 2.7 × 10^9 M^{-1} s^{-1}.

Acetophenone quenching of *W(CNdipp)$_6$ in THF.

1.5 mL of a stock solution of W(CNdipp)$_6$ (< 5 μM) in THF was added to four separate cuvettes. 0, 2, 4, and 8 μL of acetophenone were added to the four cuvettes, giving final

concentrations of 0, 11.4, 22.8, and 45.4 mM acetophenone, respectively. Excited state lifetimes were then determined for each sample.

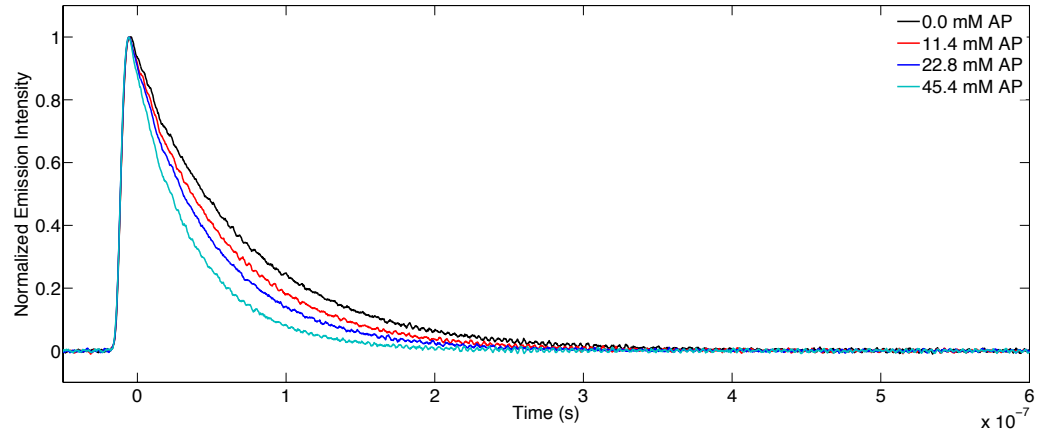

Figure S13. Quenching of *W(CNdipp)$_6$ with different concentrations of acetophenone. Wes-2-140

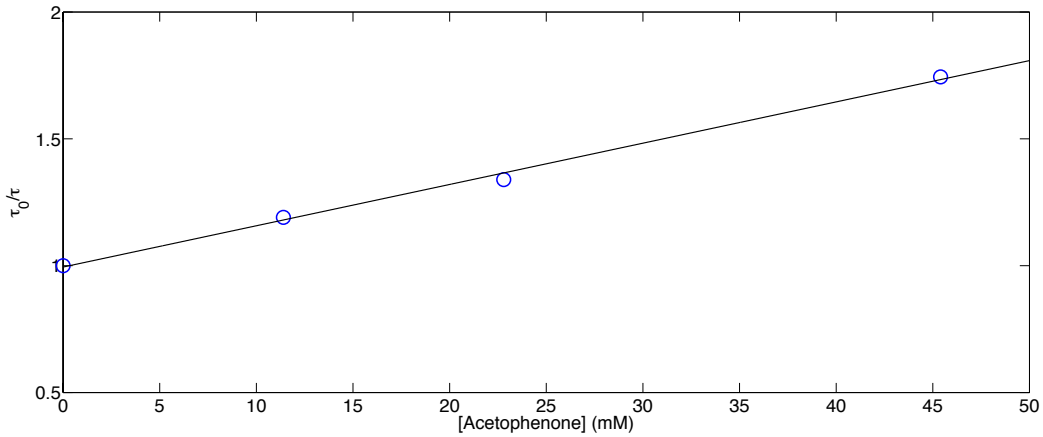

Figure S14. Plot of acetophenone concentration (mM) vs. $(\tau_0/\tau) - 1$ for W(CNdipp)$_6$ to give a quenching rate constant of 2.2 $\times 10^8$ M^{-1} s^{-1}.

Acetophenone quenching of *W(CNdippPh^{OMe2})$_6$ in THF.

1.5 mL of a stock solution of W(CNdippPh^{OMe2})$_6$ (< 5 μM) in THF was added to four separate cuvettes. 0, 100, 200, and 300 μL of acetophenone were added to the four cuvettes, giving final concentrations of 0, 535, 1007, and 1426 mM acetophenone, respectively. Excited state lifetimes were then determined for each sample.

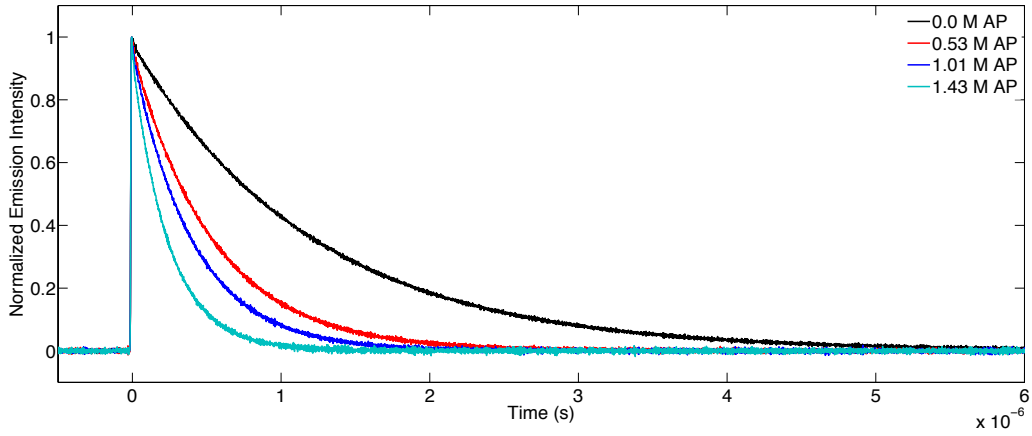

Figure S15. Quenching of *W(CNdippPh^{OMe2})$_6$ with different concentrations of acetophenone. Wes-2-140

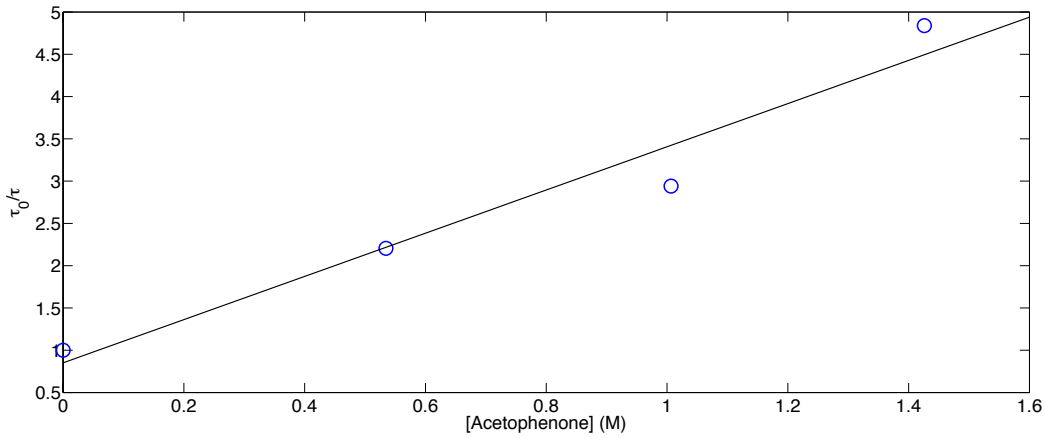

Figure S16. Plot of acetophenone concentration (M) vs. $(\tau_0/\tau) - 1$ for W(CNdippPh^{OMe2})$_6$ to give a quenching rate constant of 2.1 $\times 10^6$ M^{-1} s^{-1}.

Cyclic Voltammetry:

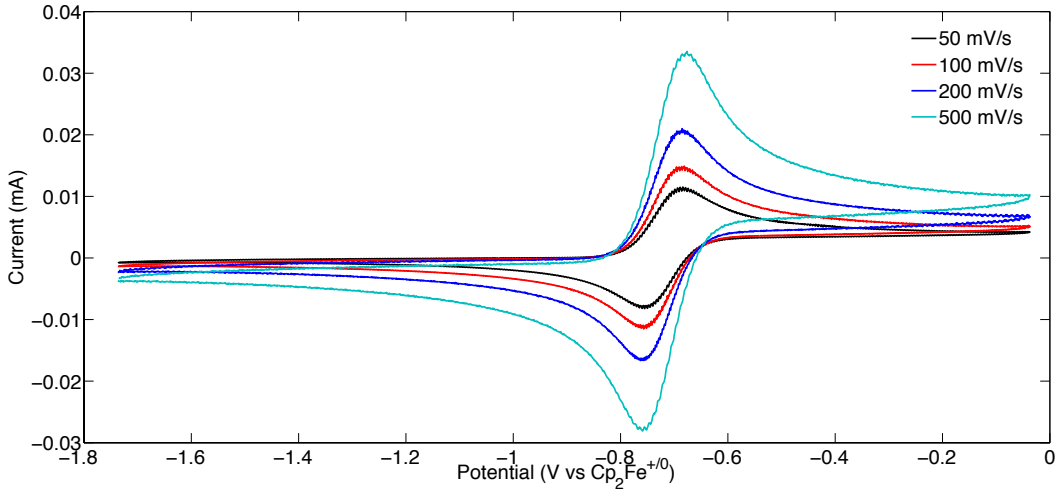

Figure S17. Cyclic voltammograms of $W(CNdipp)_6$ in 0.5 M CH_2Cl_2 solution of $[^nBu_4N][PF_6]$ at different scan rates.

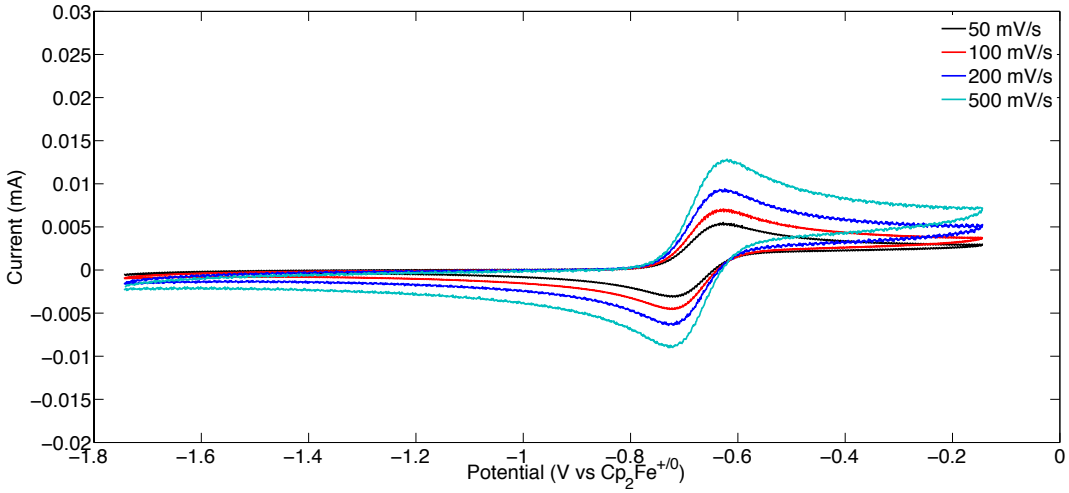

Figure S18. Cyclic voltammograms of $W(CNdippPh)_6$ in 0.5 M CH_2Cl_2 solution of $[^nBu_4N][PF_6]$ at different scan rates.

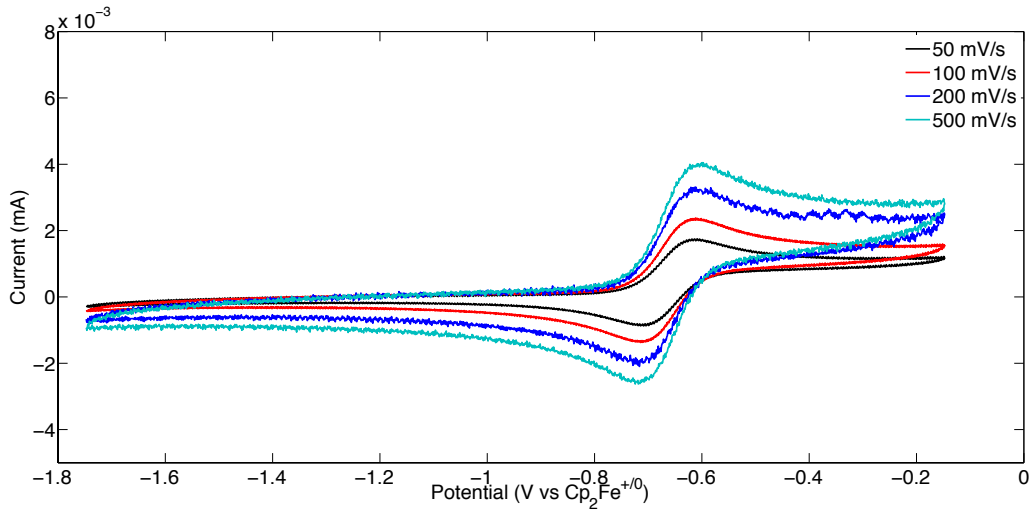

Figure S19. Cyclic voltammograms of $W(CNdippPh^{Ph})_6$ in 0.5 M CH_2Cl_2 solution of $[^nBu_4N][PF_6]$ at different scan rates.

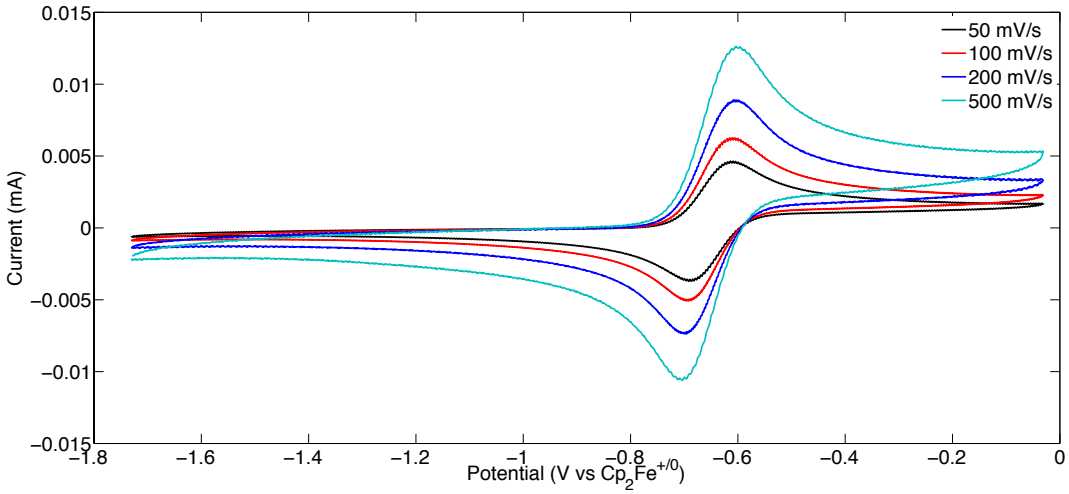

Figure S20. Cyclic voltammograms of $W(CNdippPh^{OMe_2})_6$ in 0.5 M CH_2Cl_2 solution of $[^nBu_4N][PF_6]$ at different scan rates.

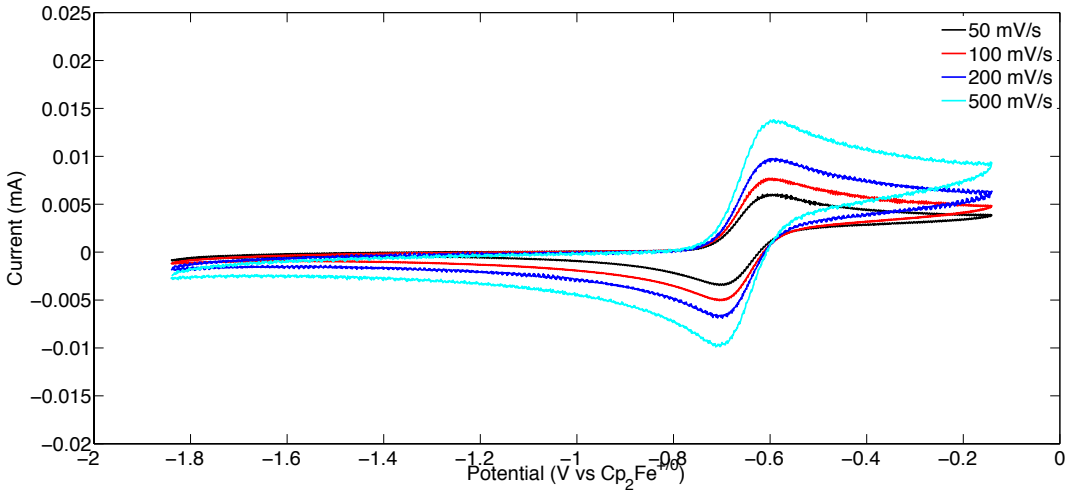

Figure S21. Cyclic voltammograms of $W(CNdippPh^{OMe_3})_6$ in 0.5 M CH_2Cl_2 solution of $[^nBu_4N][PF_6]$ at different scan rates.

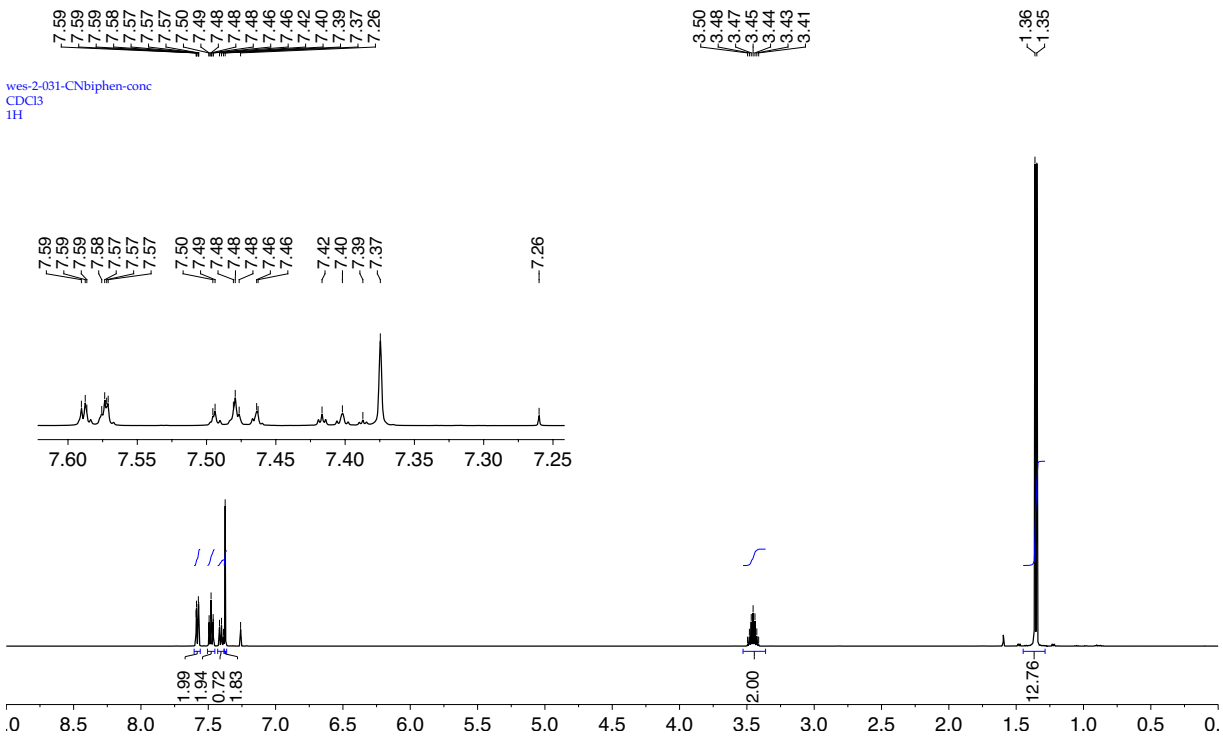

Figure S22. ^{1}H NMR spectrum of CNdippPh in $CDCl_3$.

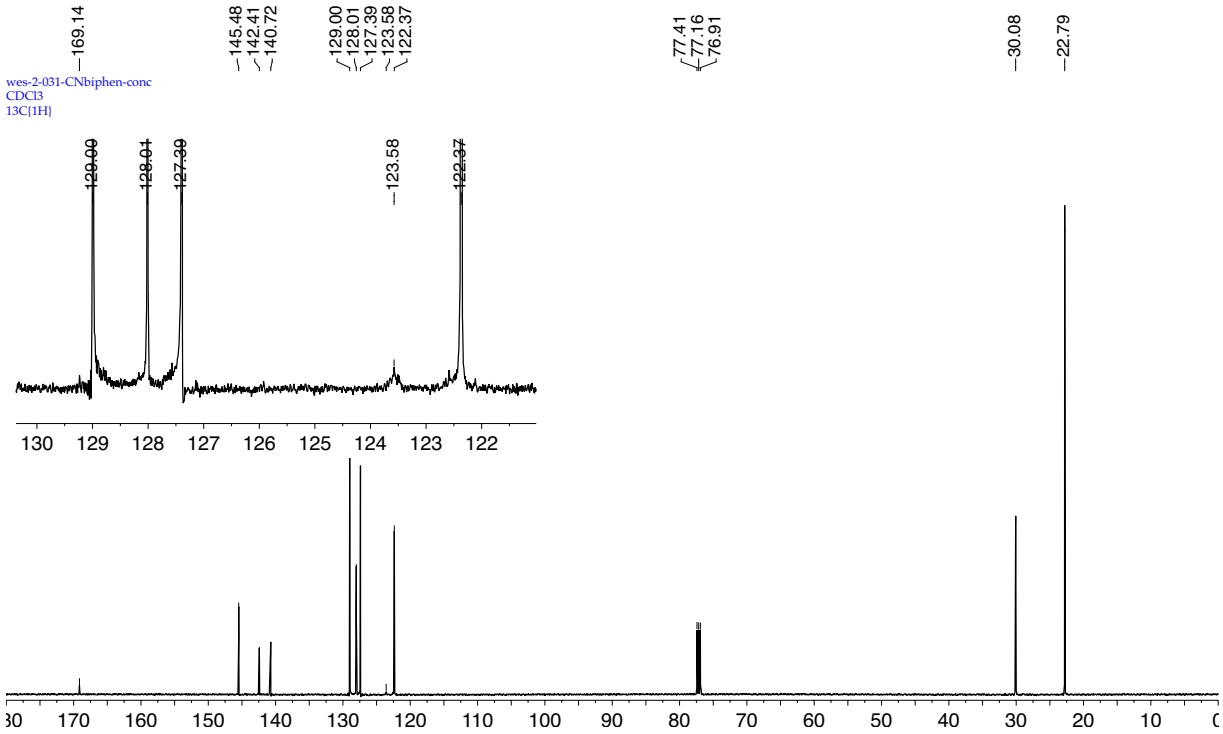

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of CNdippPh in $CDCl_3$.

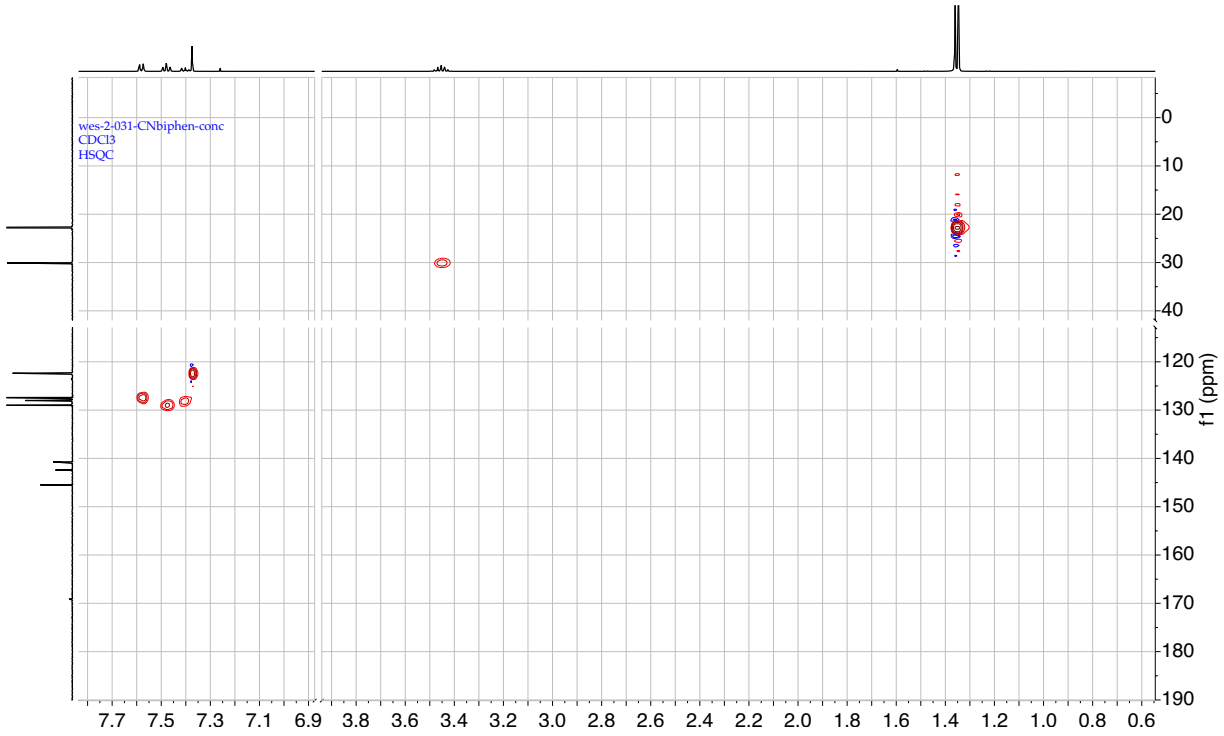

Figure S24. HSQC NMR spectrum of CNdippPh in $CDCl_3$.

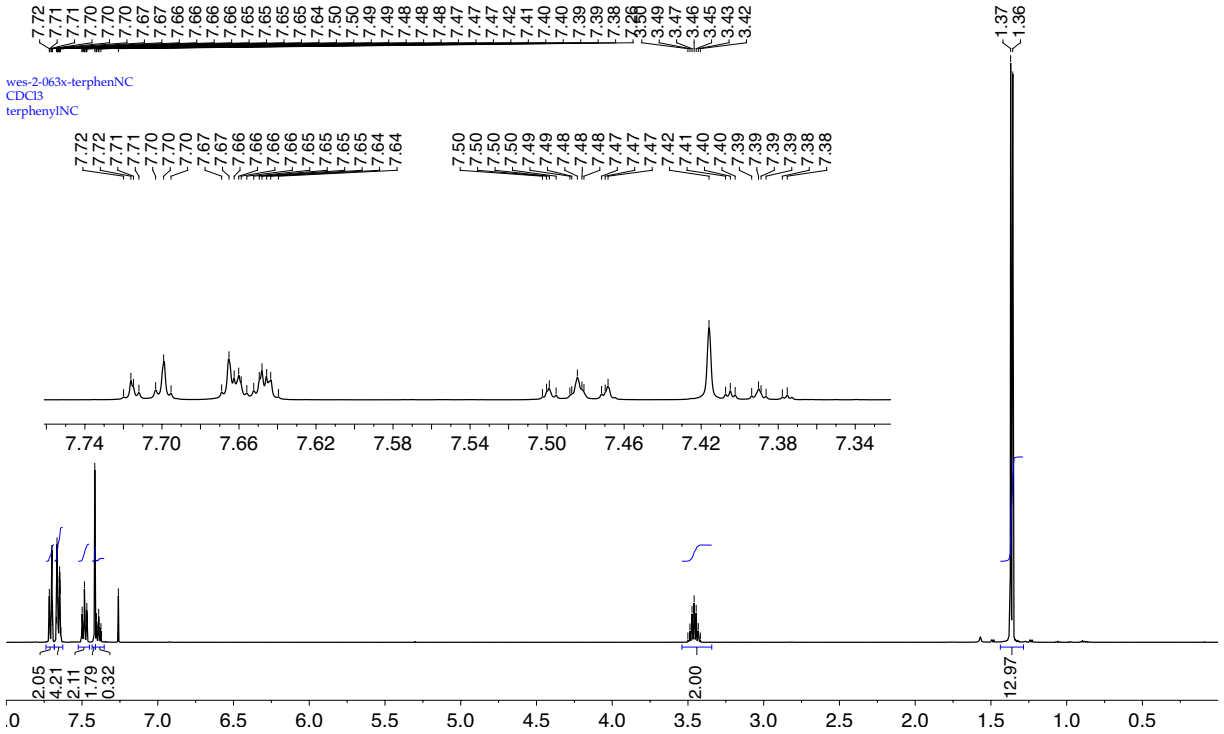

Figure S25. ^{1}H NMR spectrum of $CNdippPh^{Ph}$ in $CDCl_3$.

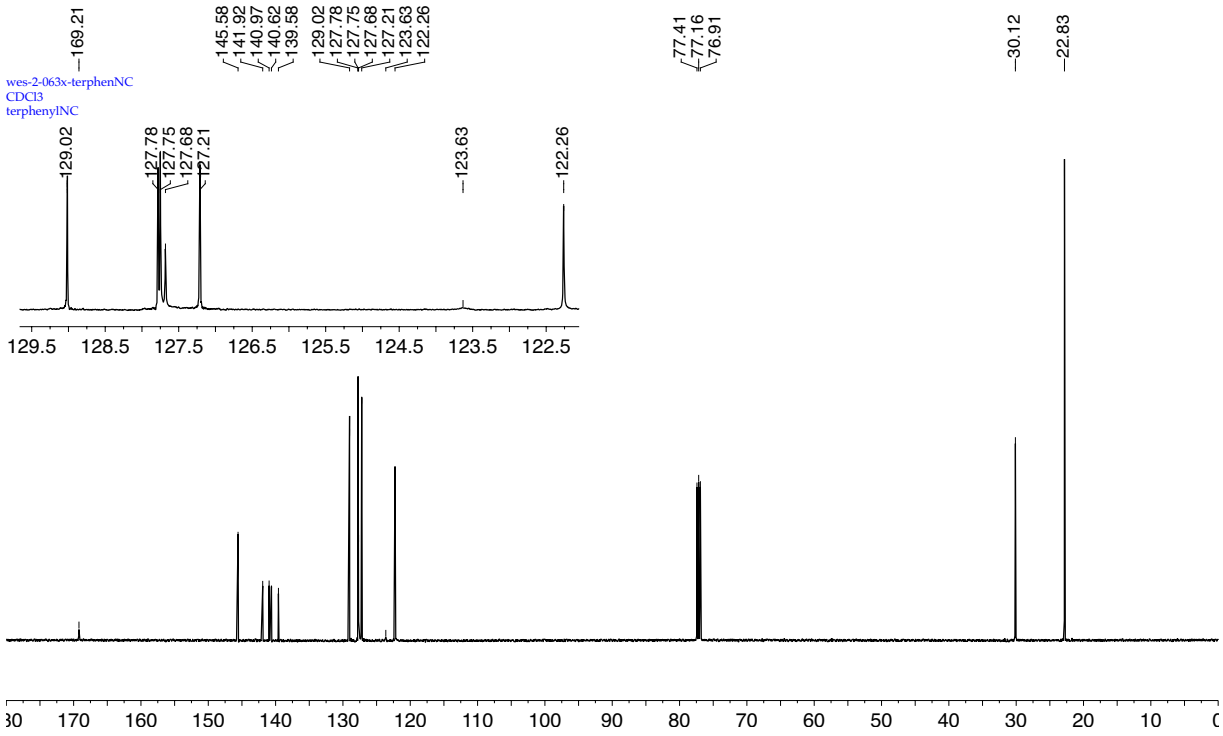

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of CNdippPh^{Ph} in $CDCl_3$.

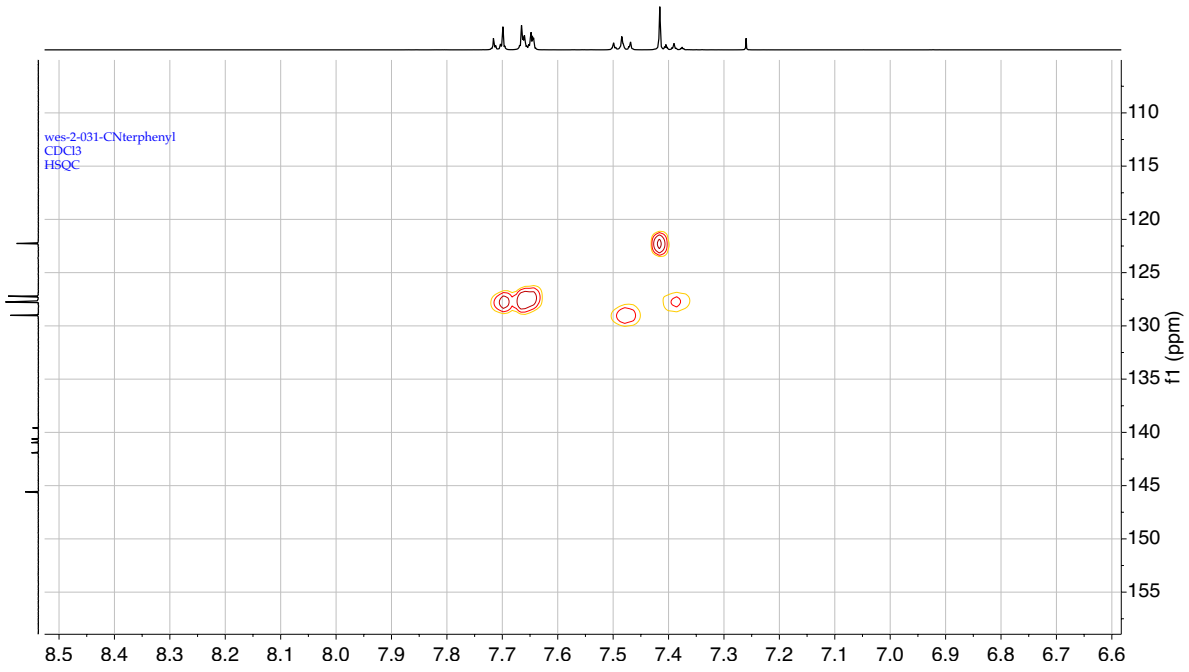

Figure S27. HSQC NMR spectrum of CNdippPh^{Ph} in $CDCl_3$.

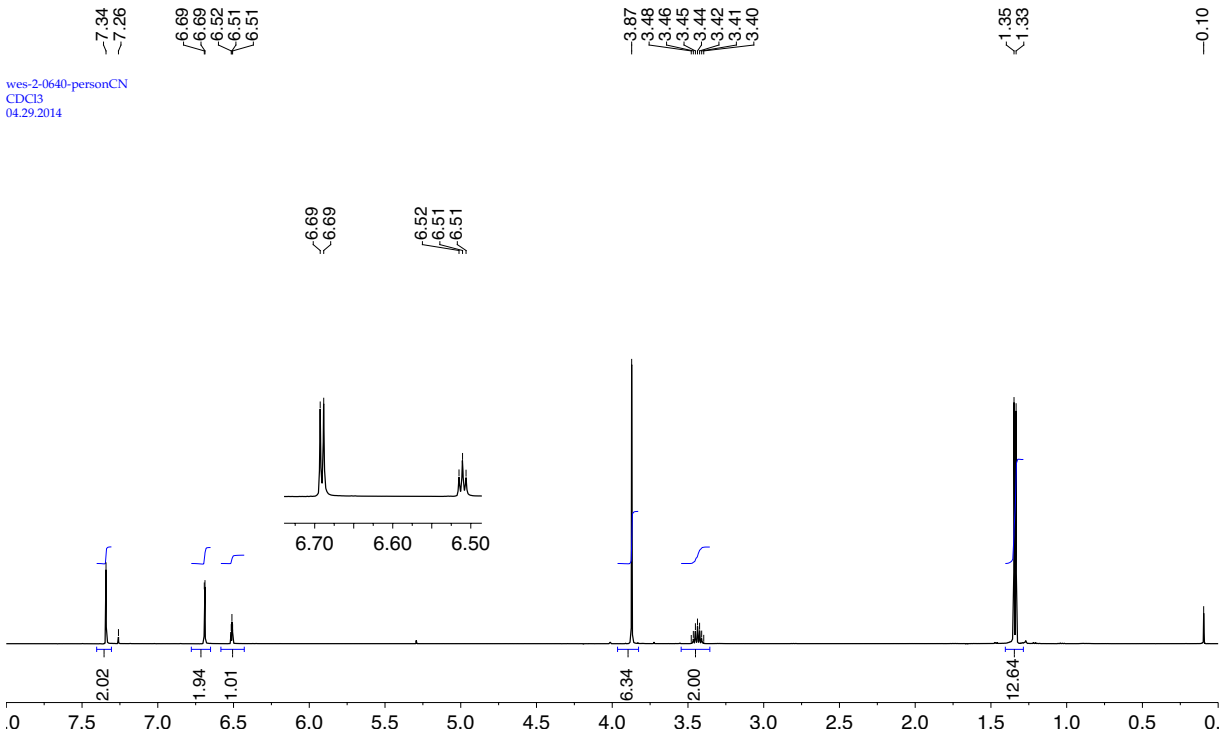

Figure S28. ^{1}H NMR spectrum of CNdippPh^{OMe2} in $CDCl_3$.

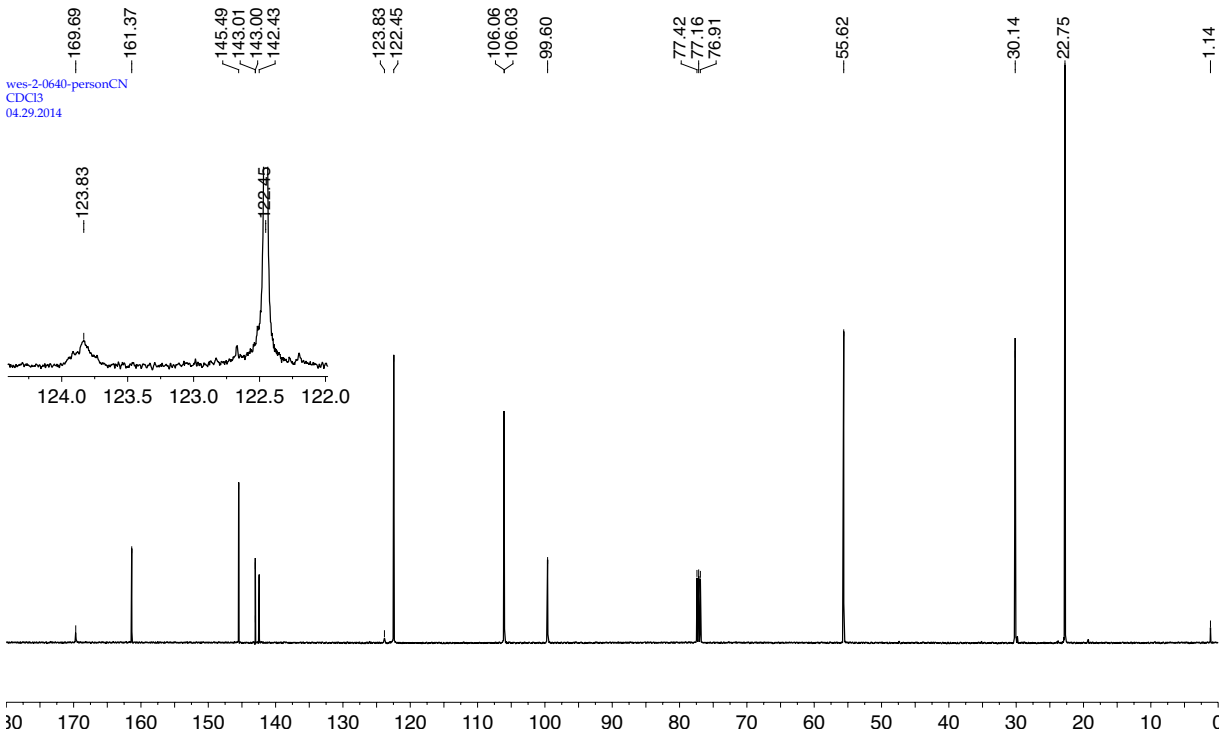

Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of CNdippPh^{OMe2} in $CDCl_3$.

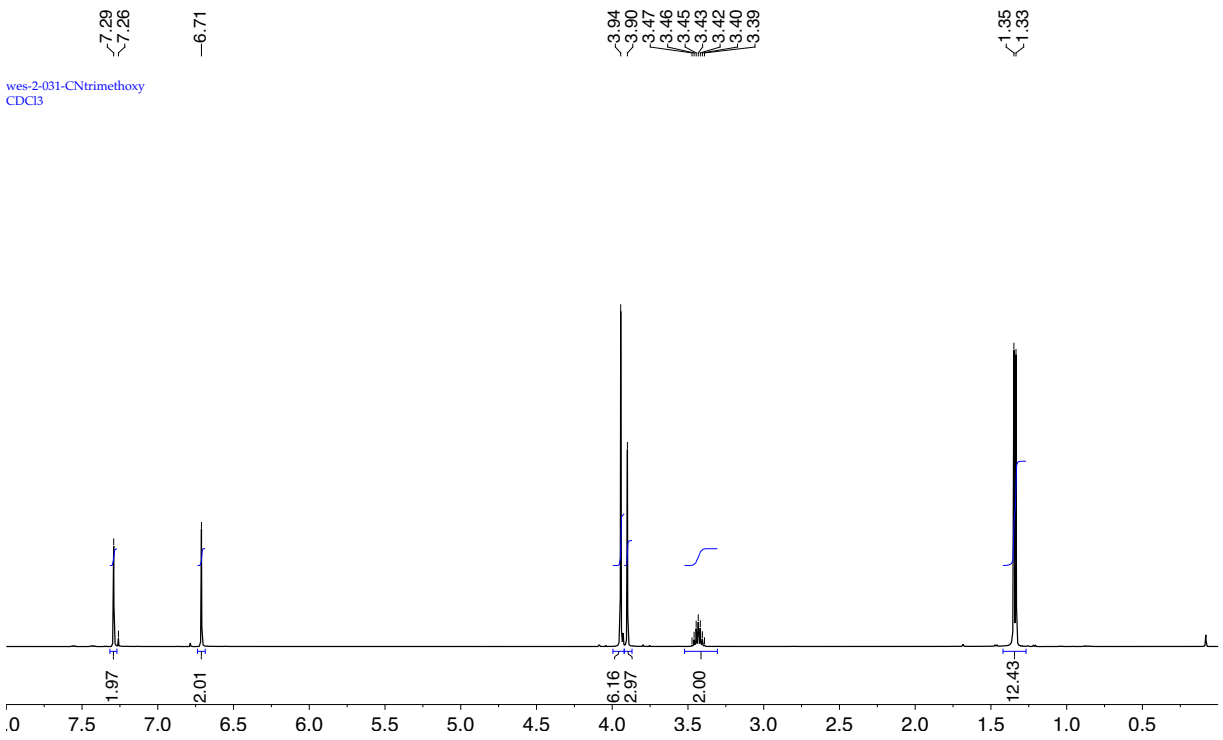

Figure S30. ^{1}H NMR spectrum of CNdippPh^{OMe3} in $CDCl_3$.

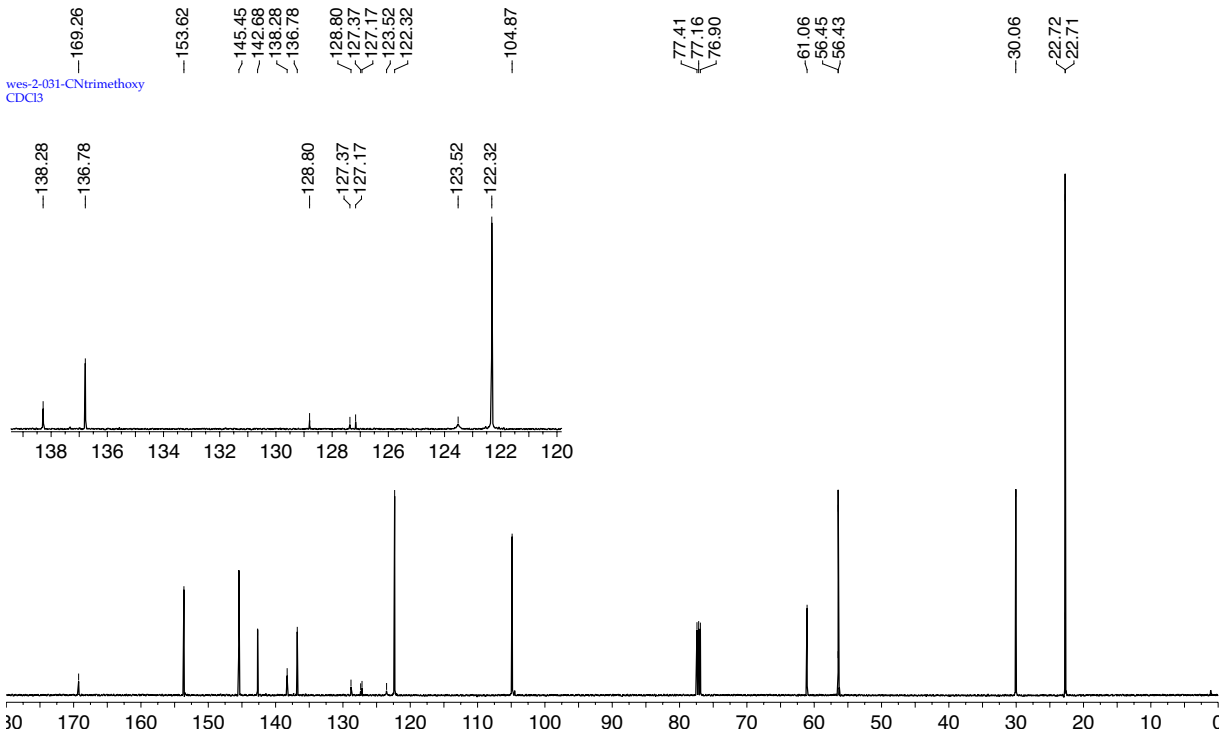

Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of CNdippPh^{OMe3} in $CDCl_3$.

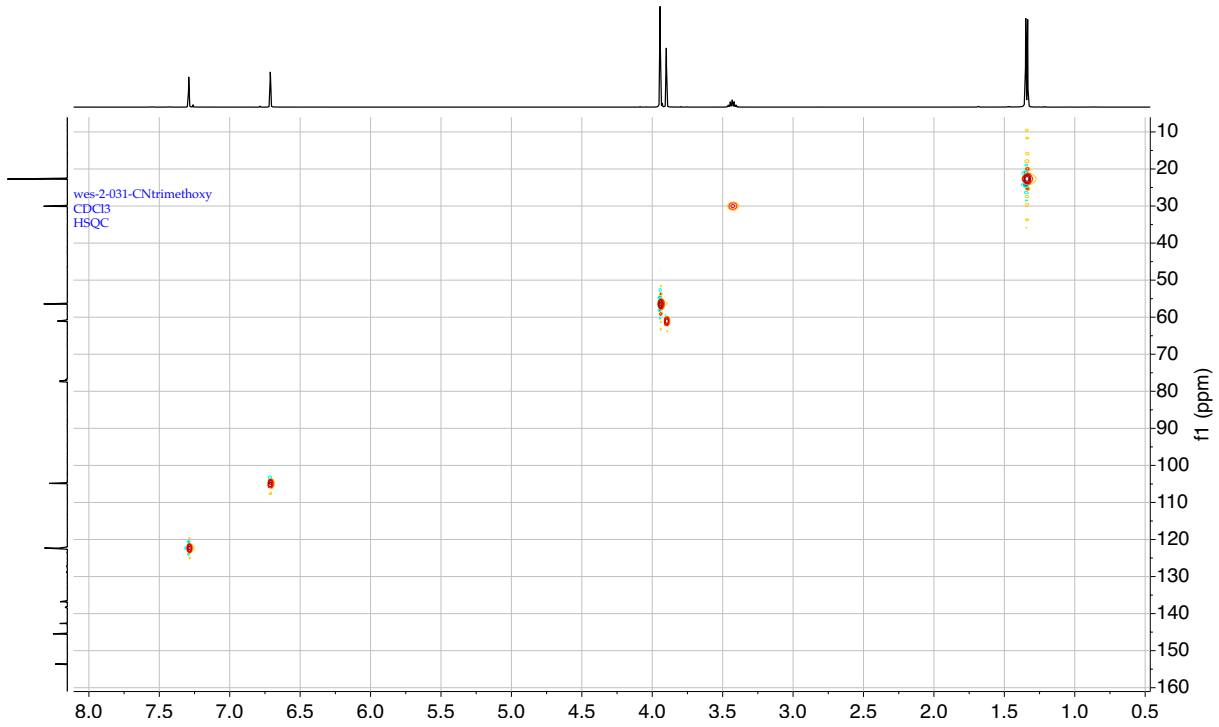

Figure S32. HSQC NMR spectrum of CNdippPh^{OMe3} in $CDCl_3$.

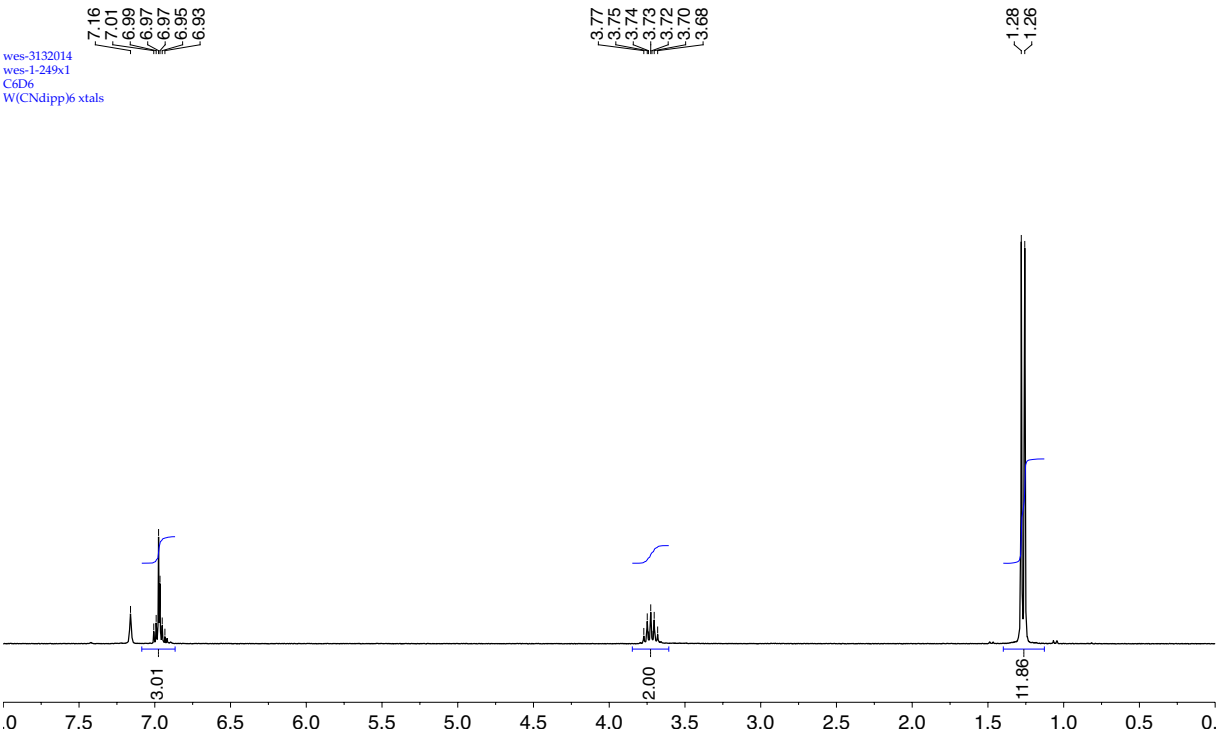

Figure S33. ^{1}H NMR spectrum of $W(CNdipp)_6$ in C_6D_6.

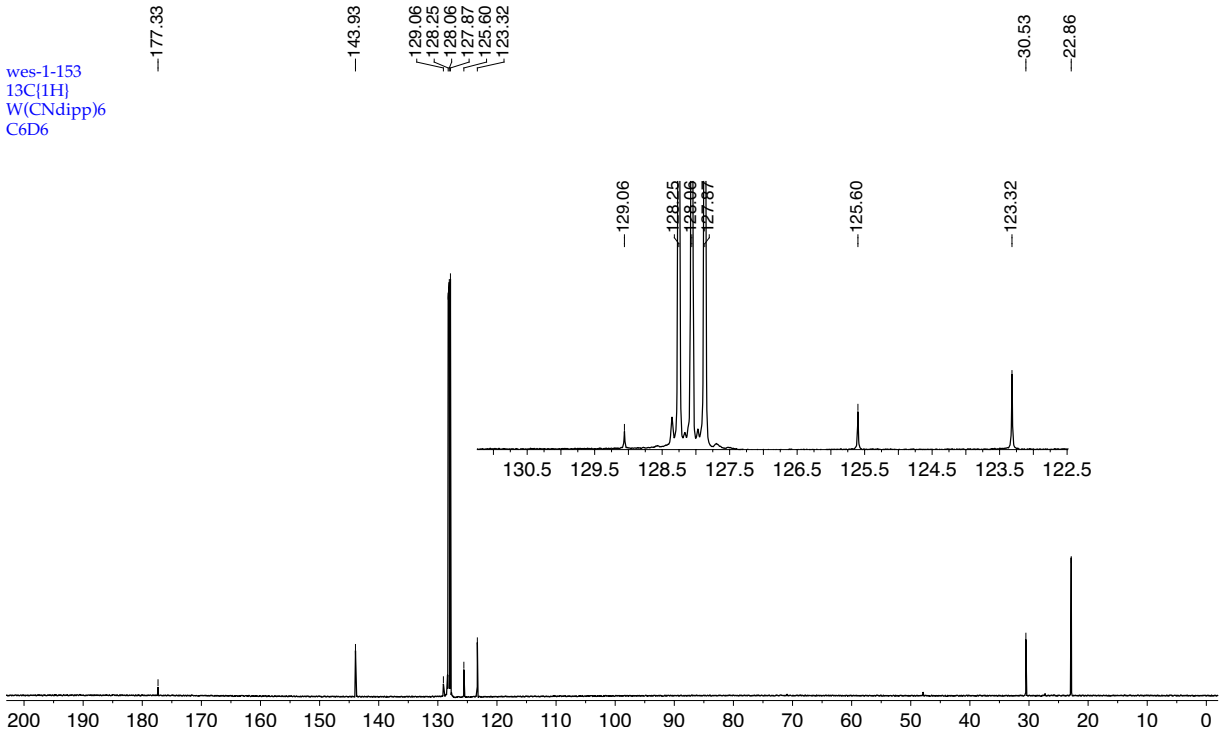

Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of $W(CNdipp)_6$ in C_6D_6.

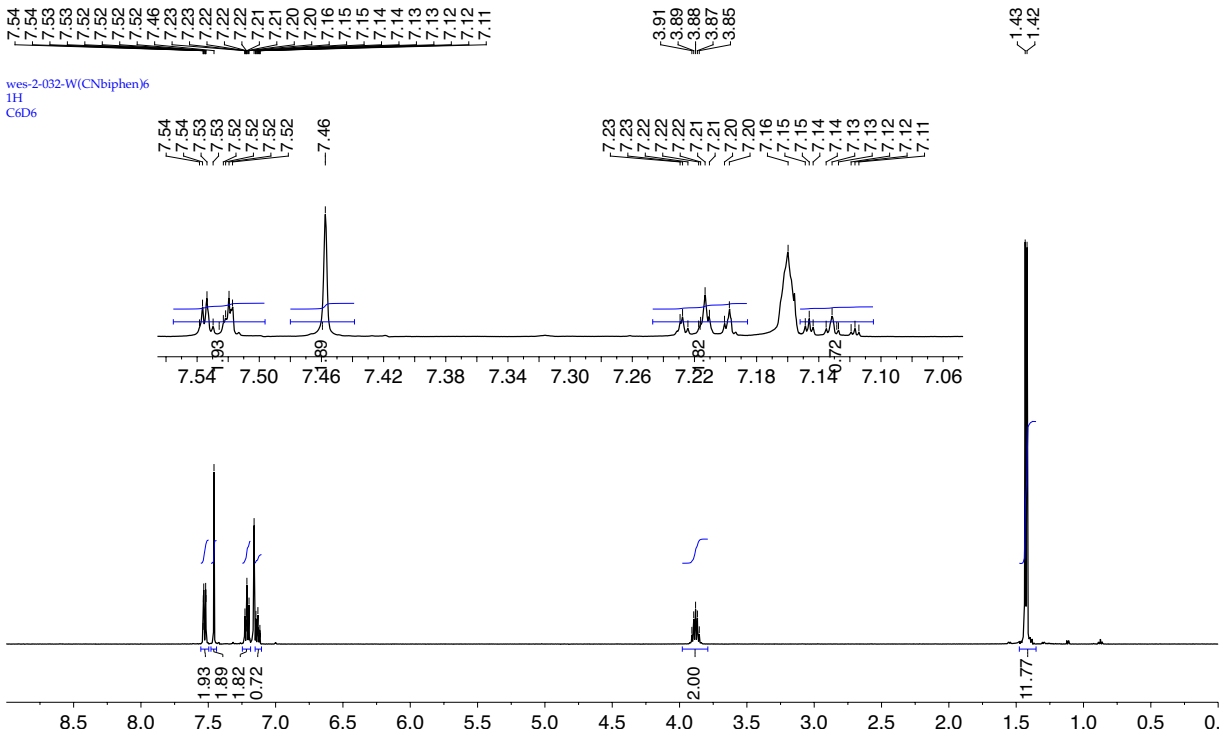

Figure S35. ^{1}H NMR spectrum of $W(CNdippPh)_6$ in C_6D_6.

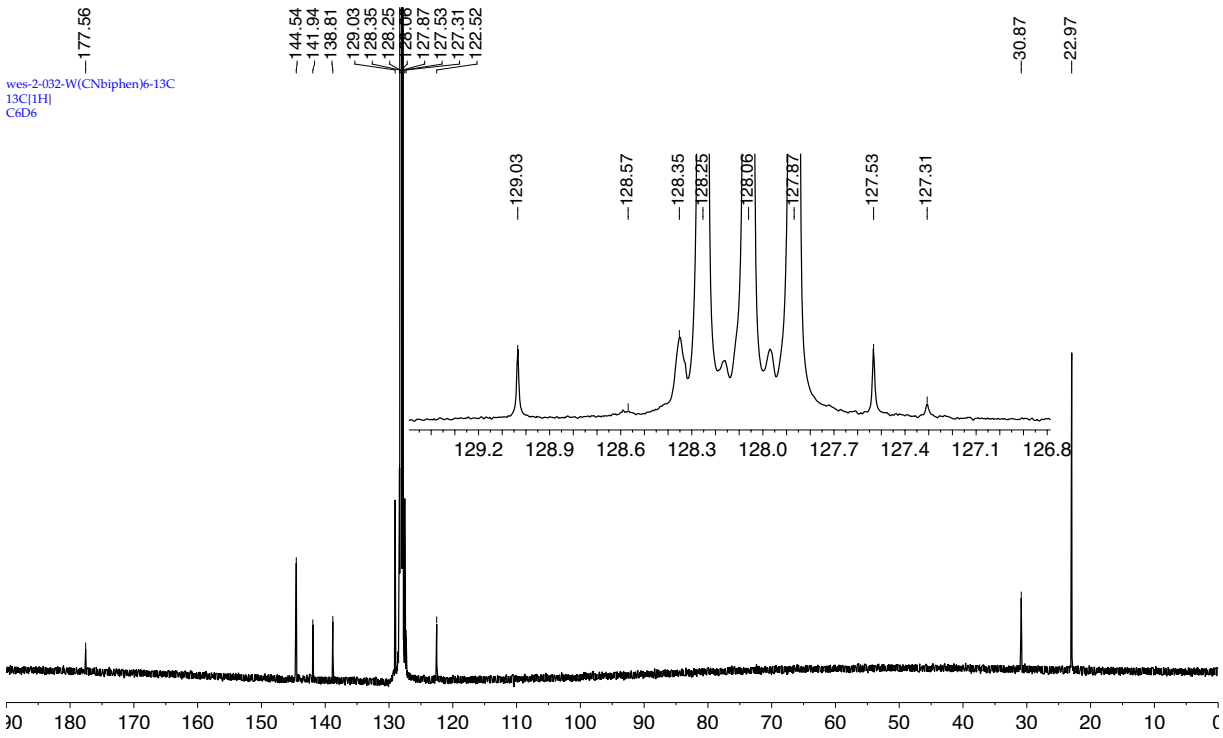

Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of $W(CNdippPh)_6$ in C_6D_6.

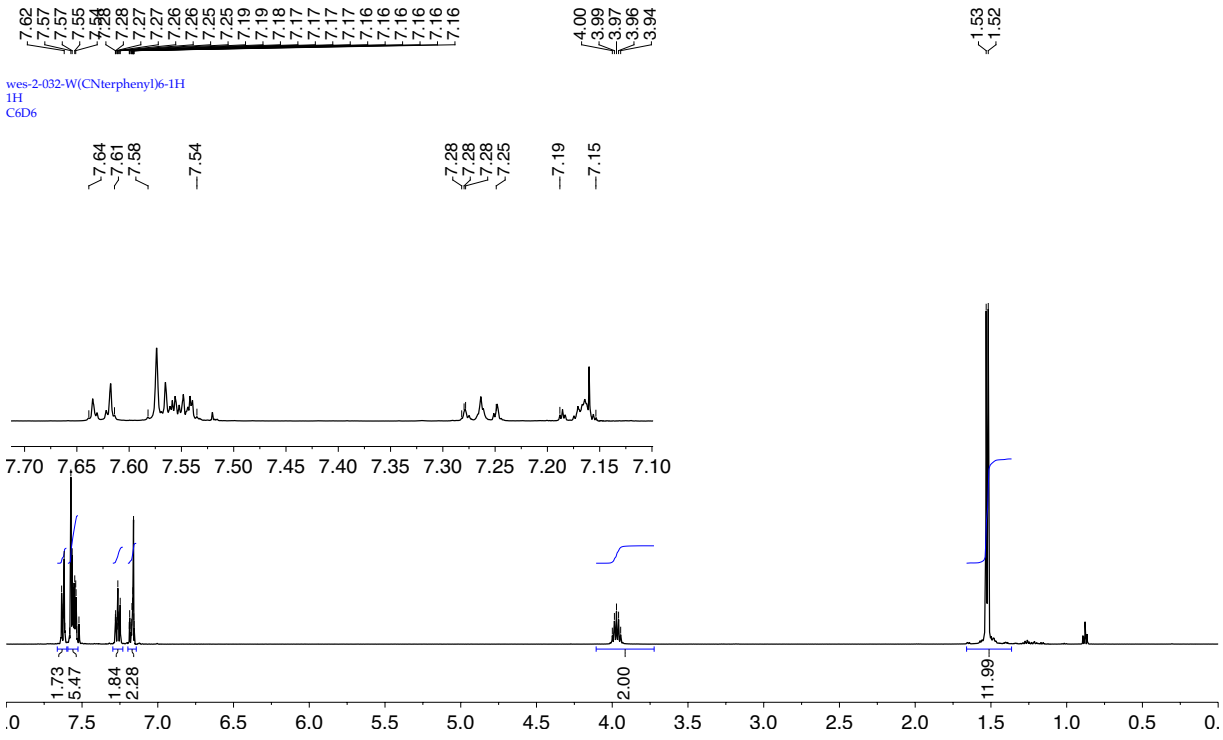

Figure S37. ^{1}H NMR spectrum of $W(CNdippPh^{Ph})_6$ in C_6D_6.

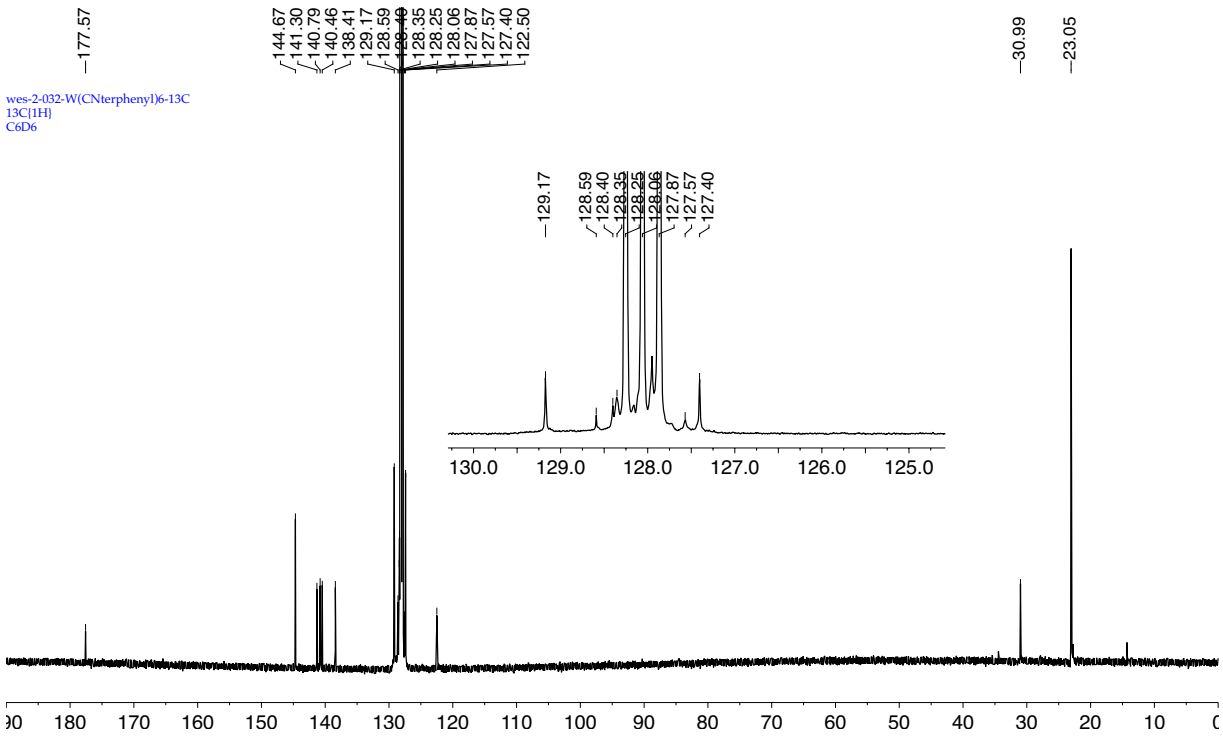

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of $W(CNdippPh^{Ph})_6$ in C_6D_6.

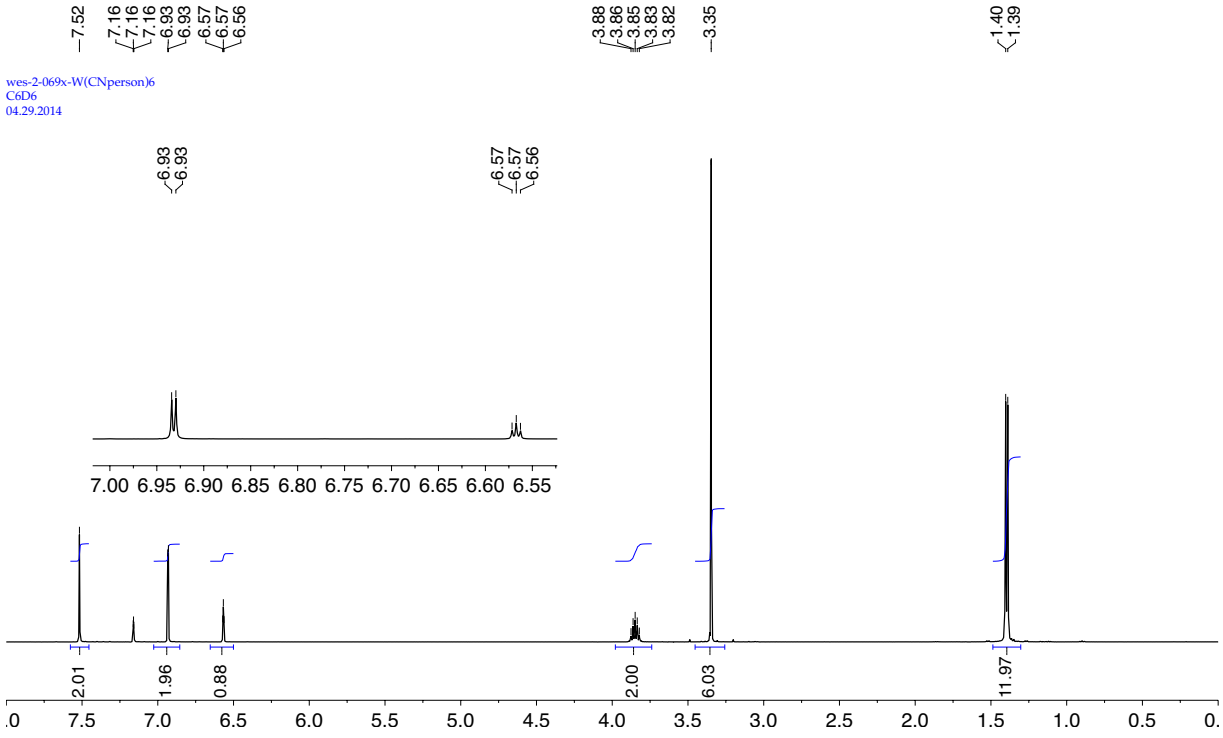

Figure S39. ^{1}H NMR spectrum of $W(CNdippPh^{OMe2})_6$ in C_6D_6.

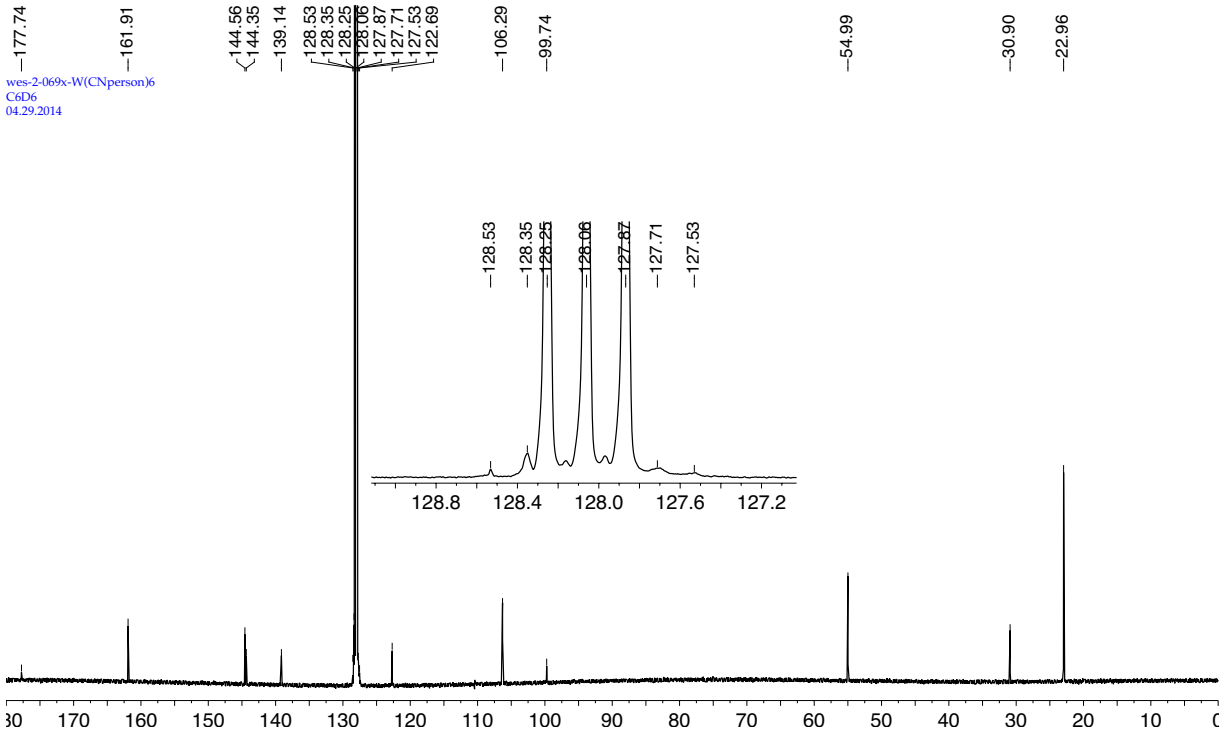

Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of $W(CNdippPh^{OMe_2})_6$ in C_6D_6.

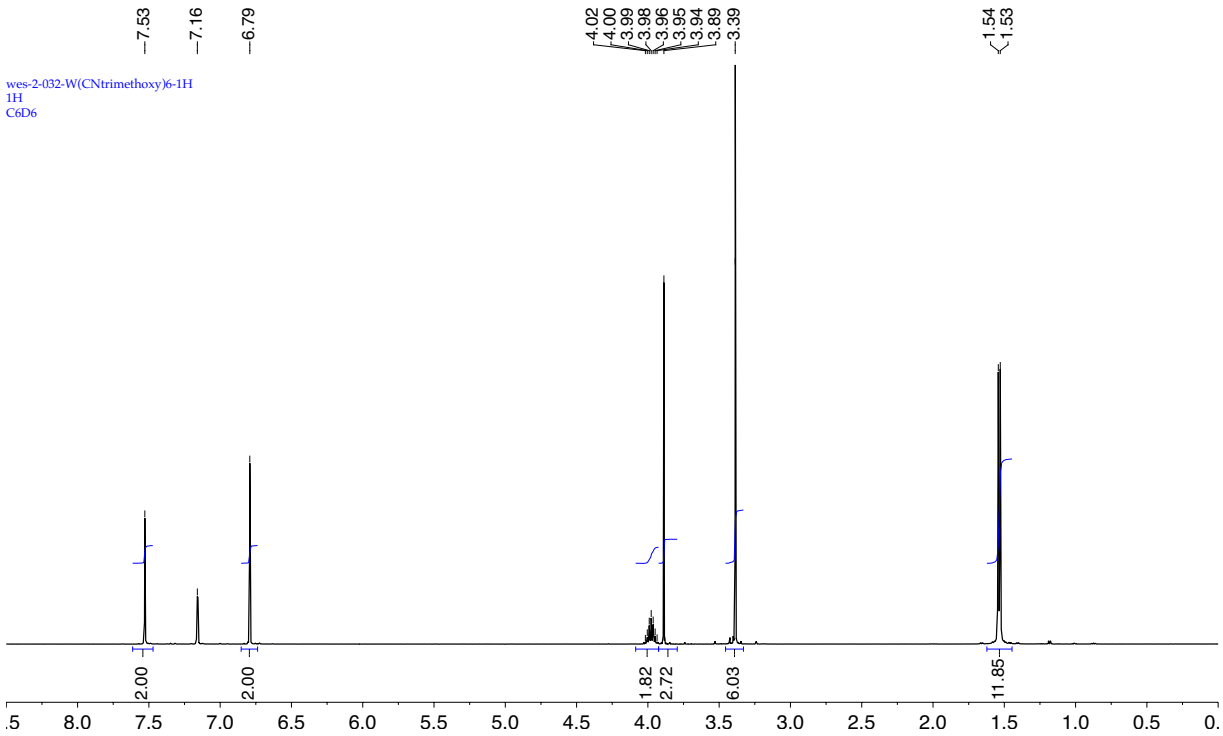

Figure S41. ^{1}H NMR spectrum of $W(CNdippPh^{OMe_3})_6$ in C_6D_6.

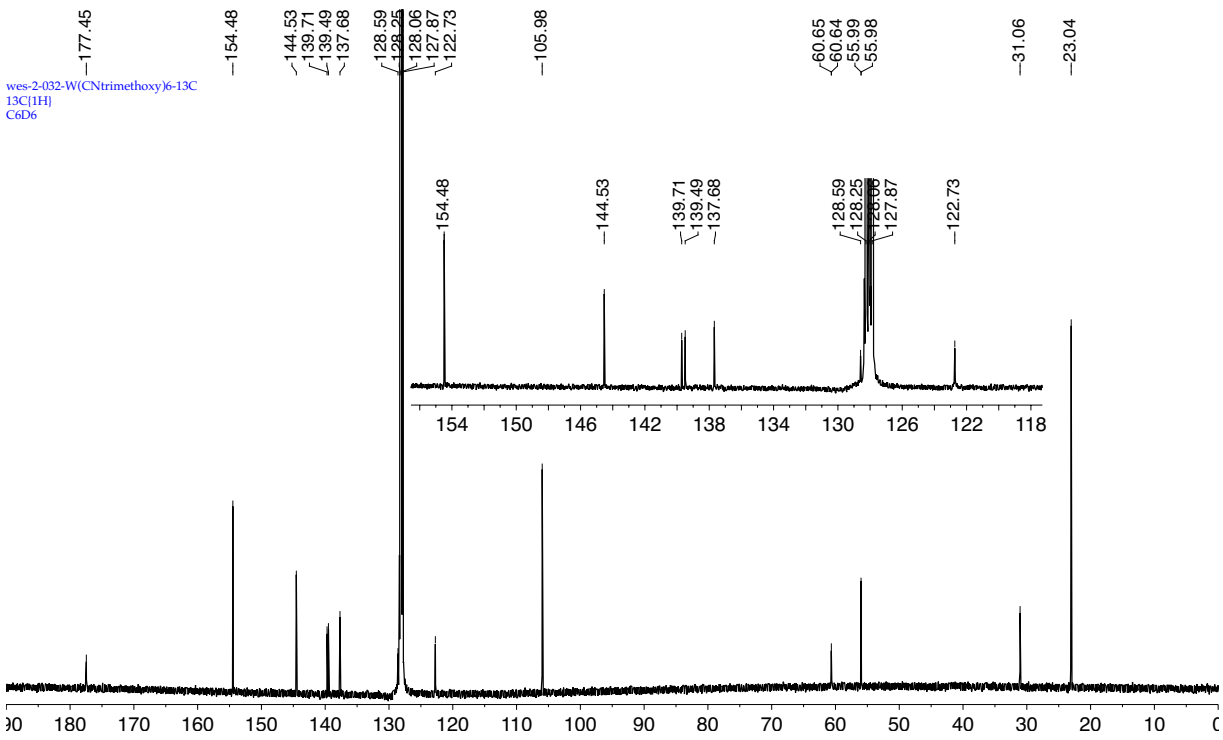

Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of $W(CNdippPh^{OMe_3})_6$ in C_6D_6.

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